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PROCEEDINGS: SYMPOSIUM ON FLUE GAS DESULFURIZATION, HELD IN ATLANTA, GEORGIA, NOVEMBER 1974. VOLUME II

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PROCEEDINGS:
SYMPOSIUM
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ATLANTA, NOVEMBER 1974
VOLUME II

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The proceedings document the presentations made during the symposium, which dealt with the status of flue gas desulfurization technology, both in the U.S. and abroad. The presentations emphasize process costs, both regenerable and non-regenerable processes, second generation processes, and byproduct disposal/utilization. Aim of the symposium was to provide potential users of sulfur oxide control technology with a current review of progress made in applying processes for the reduction of sulfur oxide emissions at the full- or semi-commercial scale. The symposium was the sixth of such EPA-sponsored meetings, dating back to 1966, when the topic of principal concern was the use of limestone to control sulfur oxide emissions.

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VOLUME II

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PREFACE

The development of technologies to control sulfur dioxide emissions is an issue of national importance. Indications that the use of sulfur-containing fossil fuels to generate electricity will increase by 50 percent by 1985, recognition that more than half of all sulfur dioxide (SO_2) emissions are caused by electric power generation, and documentation of the deleterious effects caused by such emissions make the acceleration of development to commercial application of SO_2 control technology one of the most important goals of the U.S. Environmental Protection Agency (EPA). The Control Systems Laboratory (CSL), as part of EPA's Office of Research and Development, has accelerated the development of flue gas desulfurization (FGD) technology so that it is now in the process of commercialization. Each year, CSL sponsors a Symposium which brings together users and developers of the technology for open exchange and discussion of their experience and results. The 1974 Symposium was held on November 4-7 at the Sheraton-Biltmore Hotel in Atlanta.

Commercial application of full-scale FGD processes was the primary topic of the Symposium which provided a means to transfer the latest information on the status, development and assessment of current FGD processes to developers, vendors, potential users, and those concerned with regulatory deadlines and enforcement. The Symposium was attended by more than 600 national and international representatives of utilities, vendors, government, and universities. One-third of the presentation was assessment and status reports from utilities which are utilizing full-scale FGD systems. Information from small- and large-scale pilot testing of alternate FGD systems, developments in FGD by-product disposal and utilization, and cost studies of FGD application completed the extensive overview of FGD technology.

In concluding remarks, it was noted by an international FGD technology consultant that the Symposium is recognized as the world's most significant conference on SO_2 pollution control by FGD technology. The growth of the FGD Symposium to this latest, widely attended, in-depth information exchange forum supports the conclusion that FGD is the only viable near-term alternative, other than the burning of clean fuels, that will permit compliance with current regulatory requirements.

The contents of these Proceedings are comprised of copies of the participating authors' papers as received. Although the papers have been reviewed and approved for publication by the Environmental Protection Agency, approval does not indicate that the contents necessarily reflect the views and/or policies of the Agency. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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CONTENTS

TITLE PAGE

VOLUME I

OPENING SESSION

Keynote Address - THE ROLE OF ENVIRONMENTAL HEALTH ASSESSMENT IN THE CONTROL OF AIR POLLUTION
John Finklea, Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 1

FLUE GAS DESULFURIZATION AND OTHER ALTERNATIVES FOR PRODUCING ELECTRICITY FROM COAL
S.J. Gage, Environmental Protection Agency, Washington, D. C. 5

STATUS OF FLUE GAS DESULFURIZATION SYSTEMS IN THE UNITED STATES
T.W. Devitt and F. Zada, PEDCo-Environmental, Inc., Cincinnati, Ohio 17

STATUS OF FLUE GAS DESULFURIZATION TECHNOLOGY IN JAPAN
J. Ando, Chuo University, Tokyo, Japan 125

COST COMPARISONS OF FLUE GAS DESULFURIZATION SYSTEMS
G.G. McGlamery and R.L. Torstrick, Tennessee Valley Authority, Muscle Shoals, Alabama 149

NON-REGENERABLE PROCESSES SESSION

EPA/RTP PILOT STUDIES RELATED TO UNSATURATED OPERATION OF LIME AND LIMESTONE SCRUBBERS
R.H. Borgwardt, Environmental Protection Agency, Research Triangle Park, North Carolina 225

LIMESTONE AND LIME TEST RESULTS AT THE EPA ALKALI SCRUBBING TEST FACILITY AT THE TVA SHAWNEE POWER PLANT
M. Epstein, Bechtel Corporation, San Francisco, California 241

OPERATIONAL STATUS AND PERFORMANCE OF THE ARIZONA PUBLIC SERVICE COMPANY FLUE GAS DESULFURIZATION SYSTEM AT THE CHOLLA STATION
L.K. Mundth, Arizona Public Service, Phoenix, Arizona 307

WET SCRUBBER OPERATING EXPERIENCE AT LA CYGNE STATION UNIT NO. 1
C.F. McDaniel, Kansas City Power and Light, Kansas City, Missouri 319

Preceding page blank

TITLE PAGE

DUQUESNE LIGHT COMPANY, PHILLIPS POWER STATION, LIME SCRUBBING FACILITY
S.L. Pernick, Jr. and R.G. Knight, Duquesne Light Company, Pittsburgh, Pennsylvania 329

THE HORIZONTAL CROSS FLOW SCRUBBER
A. Weir, Jr., J.M. Johnson, D.G. Jones, and S.T. Carlisle, Southern California Edison, Rosemead, California 357

OPERATIONAL STATUS AND PERFORMANCE OF THE LOUISVILLE FGD SYSTEM AT THE PADDY'S RUN STATION
R.P. Van Ness, Louisville Gas and Electric Company, Louisville, Kentucky 389

DISPOSAL OF BY-PRODUCTS FROM NON-REGENERABLE FLUE GAS DESULFURIZATION SYSTEMS
J. Rossoff, R.C. Rossi, L.J. Bornstein, The Aerospace Corporation, El Segundo, California

J.W. Jones, Environmental Protection Agency, Research Triangle Park, North Carolina 399

AN OVERVIEW OF DOUBLE ALKALI PROCESSES FOR FLUE GAS DESULFURIZATION
N. Kaplan, Environmental Protection Agency, Research Triangle Park, North Carolina 445

INITIAL OPERATING EXPERIENCES WITH A DUAL-ALKALI SO_2 REMOVAL SYSTEM
PART I - PROCESS PERFORMANCE WITH A COMMERCIAL DUAL-ALKALI SO_2 REMOVAL SYSTEM
T.T. Dingo, General Motors Corporation, Parma, Ohio 517

PART II - EQUIPMENT PERFORMANCE WITH A COMMERCIAL DUAL-ALKALI SO_2 REMOVAL SYSTEM
E.J. Piasecki, General Motors Corporation, Parma, Ohio 539

EPA-ADL DUAL ALKALI PROGRAM--INTERIM RESULTS
C.R. LaMantia, R.R. Lunt, J.E. Oberholtzer, E.L. Field, Arthur D. Little, Inc., Cambridge, Massachusetts

N. Kaplan, Environmental Protection Agency, Research Triangle Park, North Carolina 549

TITLE PAGE

VOLUME II

REGENERABLE PROCESSES SESSION

NEW ENGLAND SO_2 CONTROL PROJECT FINAL RESULTS
G.R. Koehler, E.J. Dober, Chemical Construction Corporation, New York, New York 671

ASSESSMENT OF PROTOTYPE OPERATION AND FUTURE EXPANSION STUDY - MAGNESIA SCRUBBING MYSTIC GENERATING STATION
C.P. Quigley, J.A. Burns, Boston Edison Company, Boston, Massachusetts 709

MAG-OX SCRUBBING EXPERIENCE AT THE COAL-FIRED DICKERSON STATION, POTOMAC ELECTRIC POWER COMPANY
D.A. Erdman, Potomac Electric Power Company, Washington, D.C. 729

POWER PLANT FLUE GAS DESULFURIZATION BY THE WELLMAN-LORD SO_2 PROCESS
PART I - THE DEAN H. MITCHELL STATION
E.L. Mann, Northern Indiana Public Service Company, Michigan City, Indiana 739

PART II - CONTINUING PROGRESS FOR THE WELLMAN-LORD SO_2 PROCESS
E.E. Bailey, Davy Powergas, Inc., Lakeland, Florida 745

THE CAT-OX DEMONSTRATION PROGRAM
E.M. Jamgochian, The Mitre Corporation, McLean, Virginia

W.E. Miller, Illinois Power Company, Decatur, Illinois 761

THE SHELL FLUE GAS DESULFURIZATION PROCESS
J.B. Pohlenz, Universal Oil Products Company, Des Plaines, Illinois 807

STATUS REPORT ON CHIYODA THOROUGHBRED 101 PROCESS
M. Noguchi, Chiyoda International Corporation, Seattle, Washington 837

FLUE GAS DESULFURIZATION BY-PRODUCT DISPOSAL/UTILIZATION PANEL

FLUE GAS DESULFURIZATION BY-PRODUCT DISPOSAL/UTILIZATION - REVIEW AND STATUS
H.W. Elder, Tennessee Valley Authority, Muscle Shoals, Alabama 851

TITLE PAGE

LIME/LIMESTONE SLUDGE DISPOSAL - TRENDS IN THE UTILITY INDUSTRY
C.N. Ifeadi and H.S. Rosenberg,
Battelle, Columbus, Ohio 865

ENVIRONMENTALLY ACCEPTABLE DISPOSAL OF FLUE GAS DESULFURIZATION SLUDGES: THE EPA RESEARCH AND DEVELOPMENT PROGRAM
J.W. Jones, Environmental Protection Agency,
Research Triangle Park, North Carolina 887

FGD SLUDGE FIXATION AND DISPOSAL
W.H. Lord, Dravo Corporation,
Pittsburgh, Pennsylvania 929

UTILIZING AND DISPOSING OF SULFUR PRODUCTS FROM THE GAS DESULFURIZATION PROCESSES IN JAPAN
J. Ando, Chuo University,
Tokyo, Japan 955

TVA-EPA STUDY OF THE MARKETABILITY OF ABATEMENT SULFUR PRODUCTS
J.I. Bucy and P.A. Corrigan,
Tennessee Valley Authority,
Muscle Shoals, Alabama 969

THE PRODUCTION AND MARKETING OF SULFURIC ACID FROM THE MAGNESIUM OXIDE FLUE GAS DESULFURIZATION PROCESS
I.S. Zonis, F. Olmsted, K.A. Holst, D.M. Cunningham,
Essex Chemical Corporation, Clifton, New Jersey 1003

SECOND GENERATION PROCESSES SESSION

SECOND GENERATION PROCESSES FOR FLUE GAS DESULFURIZATION - INTRODUCTION AND OVERVIEW
A.V. Slack, SAS Corporation, Sheffield, Alabama 1029

PILOT PLANT TESTING OF THE CITRATE PROCESS FOR SO_2 EMISSION CONTROL
W.A. McKinney, W.I. Nissen, D.A. Elkins and
J.B. Rosenbaum, Bureau of Mines,
Salt Lake City, Utah 1049

TVA-EPA PILOT-PLANT STUDY OF THE AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PROCESS
C.E. Breed, Tennessee Valley Authority,
Muscle Shoals, Alabama

G.A. Hollinden, Tennessee Valley Authority,
Chattanooga, Tennessee 1069

TITLE PAGE

DESCRIPTION AND OPERATION OF THE STONE & WEBSTER/IONICS SO_2 REMOVAL AND RECOVERY PILOT PLANT AT THE WISCONSIN ELECTRIC POWER COMPANY VALLEY STATION IN MILWAUKEE
K.A. Meliere and R.J. Gartside, Stone & Webster Engineering Corporation, Boston, Massachusetts

W.A. McRae and T.F. Seamans, Ionics, Inc., Waltham, Massachusetts 1109

CALSOX SYSTEM DEVELOPMENT PROGRAM PRESENTED AT THE EPA FLUE GAS DESULFURIZATION SYMPOSIUM
R.E. Barnard and R.K. Teague, Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri

G.C. Vansickle, Indianapolis Power & Light Company, Indianapolis, Indiana 1127

WESTVACO ACTIVATED CARBON PROCESS FOR SO_x RECOVERY AS ELEMENTAL SULFUR
F.J. Ball, G.N. Brown, A.J. Repik, S.L. Torrence, Westvaco Corporation, North Charleston, South Carolina 1151

NEW ENGLAND SO_2 CONTROL PROJECT

FINAL RESULTS

BY

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Prepared For Presentation At
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NEW ENGLAND SO_2 CONTROL PROJECT

FINAL RESULTS

George R. Koehler*
Edward J. Dober

INTRODUCTION

Operational testing of the Magnesia Slurry System for SO_2 control has been completed in a full size, prototype plant employing a single stage venturi absorber for SO_2 and particulate removal. This Chemico-Basic System treated all the flue gas from an oil fired boiler powering a 150 MW generator at Boston Edison Company's Mystic Station.

The program spanned a 21 month period for the construction of the plants and an additional 27 month period of operation in which over 4,000 hours of running time on the absorption system were logged. During the operating period, it was demonstrated that:

1) The process could remove SO_2 and particulate from a high sulfur fuel oil flue gas.
2) The basic concepts of the system were sound.
3) Process guarantees of 90% removal of the inlet SO_2 could be met, and particulate removal could be achieved.
4) Magnesia could be regenerated and recycled. During the course of the program over 6,800 tons of $MgSO_3$ was processed, and more than 3,000 tons of magnesia regenerated and recycled.
5) 98% sulfuric acid of high quality could be recovered from the SO_2 removed in the pollution abatement plant. Over 5,000 tons of 98% sulfuric acid was produced from $MgSO_3$ and marketed in the conventional manner.

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INTRODUCTION continued

In addition, operation of the full size plant yielded valuable information for the design of future plants:

1) A correlation was developed allowing prediction and process control of SO_2 removal for other design requirements.
2) A correlation was developed allowing prediction and process control of the regeneration plant to produce magnesia suitable for recycle.
3) Studies of the complex physio-chemistry of the process were undertaken yielding data, not previously reported on:
    a) The kinetics of the $MgSO_3$ hydrate formation and transformation.
    b) The activation phenomena of regenerated MgO slaking.
    c) The formation and influence of $MgSO_4$ in the system.
4) Measurements of the physical properties of the chemical components of the system were made.
5) New analytical methods and techniques were developed to assure process and quality control at the plants.
6) Observation and testing of the suitability of the equipment and materials of construction yielded new recommendations for the design of improved plants.

Finally, the accumulation of operating experience and a large data bank for reference allowed initiation of the second phase of the overall application of the magnesia slurry system for SO_2 control at a coal fired generating station.

REVIEW OF INSTALLED FACILITIES

A Chemico-Basic magnesia SO_2 absorption system (Fig. 1) was installed on a fuel oil fired boiler at Boston Edison Company's Mystic Station. The absorber and related equipment was "retrofitted" to the 156 MW unit No. 6 of the station, which has a Combustion Engineering controlled circulation,tangentially fired boiler. This boiler is rated to produce 1,000,000#/hr. of steam at 1800 psig, and 1000°F with reheat to 1000°F firing 9700 GPH of #6 fuel oil.

The equipment "retrofitted" on the Mystic #6 boiler was:

1) Two new 800 H.P. booster fans.
2) Single stage venturi absorber and slurry recycle pumps and lines.
3) Centrifuge system including centrate tank.
4) Dryer.
5) MgO storage silo (an existing ash silo was modified for $MgSO_3$ storage).
6) MgO make-up system, including weigh feeder, slurry tank, and pumps.
7) Interconnecting materials handling equipment.

The venturi absorber is a co-current gas contactor, 31' in diameter by 50 ft. overall height with a double annular throat. The absorber was designed for optimum dispersed absorbing surface at a gas flow of 425,000 A.C.F.M. In actual operation, however, the absorber had to treat as much as 650,000 A.C.F.M. because of a high leakage in the existing boiler ductwork.

The regeneration section of the Chemico-Basic process was added to a sulfuric acid plant with a nominal output of 50 TPD of 98% sulfuric acid. The Essex Chemical acid plant is located in Rumford, R.I., and had been supplying sulfuric acid for industrial uses since 1928 when it was built by Chemico. Some modifications to the acid plant were necessary to allow it to take SO_2 produced during the regeneration of magnesia as its feed.

REVIEW OF INSTALLED FACILITIES continued

The regeneration facilities are comprised of feed $MgSO_3$ and product MgO storage silos (again, an existing soda ash silo was used for bulk $MgSO_3$ storage), coke storage, metering equipment for coke and $MgSO_3$ feed, a direct fired, refractory lined, rotary calciner 7'6" ID x 120' long, and interconnecting materials handling equipment. A gas cleaning and conditioning system consisting of a hot cyclone, followed by a venturi scrubber for particulate removal and a separator - cooler and related heat exchange equipment to reduce the gas temperature to 100°F, is also included in the system.

Acid plant modifications were limited to: a new main blower to provide both suction for the regeneration plant and pressure for the acid plant, a "cold heat exchanger", and small gas stripping towers.

Recently, operation of a similar SO_2 and particulate control system has been started at Potomac Electric Power Company's Dickerson Station. Again, a Chemico Basic magnesia system was retrofitted on their unit No. 3. This is a coal fired boiler, and the SO_2 absorption system was installed so that it could treat the flue gas taken off either before or after the electrostatic precipitators.

The system installed on PEPCO's unit No. 3 is similar to the Boston design, differing in these important areas:

Flue gas is first treated for particulate removal in a 1st stage venturi scrubber. This unit, while it has been installed in the same shell as the venturi absorber is a separate fly ash removal system with its own thickener, slurry pumps and piping for fly ash slurry handling.

REVIEW OF INSTALLED FACILITIES continued

After particulate removal, the gas passes to the SO_2 removal stage. A single 3500 HP fan, designed for 290,000 ACFM, is placed after the absorber and provides the pressure drop for the system. This is a "wet" fan design, and is followed by a mist eliminator vessel before the gas returns to the stack.

The same regeneration plant, at Rumford, R.I., is used for this installation.

PROGRESS

(The progress of the work which was accomplished to mid 1973 has been reported in several previous papers (1 - 6). The object of this paper is to describe the work undertaken during the last year of the project, to establish the significant findings and to describe the correlations which have been developed from the data).

By June 1973, most system modifications had been made. One remaining problem area, the formation of hard deposits in the dryer conveyor where the cyclone underflow was reintroduced, was eliminated by installing a pneumatic conveying system to take the dry dust directly to the product silo. The spill back hopper was also serviced by this system eliminating an MgO loss point. The series of improvements made to the dryer converted it to a partial granulator which allowed it to handle either the magnesium sulfite hexa or trihydrate.

One further attempt at improvement was made when one of the four dryer cyclones in the multiple array was blocked off to increase the unit's efficiency at the Boston Edison Plant.

The result was so successful that the increase in collected dust overloaded the conveying system. The baffle was removed and the unit returned to its original condition.

One other modification was also made at Rumford in August 1973. The $MgSO_3$ elevator was converted from a centrifugal to a continuous discharge type. This immediately reduced the "recycling" that had caused elevator "trip outs" and plant shut downs in previous attempts to operate with the dusty feed sometimes introduced.

PROGRESS continued

Attempts to achieve longer operational periods during the remainder of the year were frustrated by a series of mechanical, material handling problems interspersed with shut downs due to boiler tube leaks. However, the first of several performance series runs was made. All of the tests confirmed the results of the previously reported continuous monitoring in that 90% SO_2 removal was attained by the system. The first tests in October also showed that the system was being called on to treat a gas flow 50% in excess of design.

Corrosion - erosion of the unprotected steel piping, valves, and pumps also caused more delays and outages were taken in August and November for repair work. Reliability was not achieved until extensive replacement of valves and pumps was undertaken in December.

Also, centrifuge inspections in August, September, and February resulted in additional delays of almost a month, as new hard facings were applied to determine which of them resulted in longer service life.

In all, for the period June 1973 thru February 1974, 1630 additional hours of absorber running time were logged with 700 of those hours in the June - July period.

By mid-February, it appeared that the magnesia system and operational staff were in their best state of readiness. Preparations were made to run performance tests and also to attempt sustained operations at the design gas flow. Permission was obtained to run the system with a partial by-pass of the excess flow for most of the following test period.

PROGRESS continued

Fig. 2 shows, in graphical form, the operations during 1974, including the four months of Operations Testing. During the period from March 8th to the end of the program on June 26th, 1350 hours of additional running time were logged, despite the large number of interruptions caused by boiler tube failures.

These numerous interruptions did demonstrate, unequivocally, that the absorption system could cycle with an operating boiler. In the 35 day period from 4/12 thru 5/10, 623 hours were logged at essentially 100% availability, despite nine interruptions caused by boiler related problems.

Performance Test Results

A condensed summary of the performance test results obtained in February 1974 are given in Tables 1 and 2.

SO_2 REMOVAL

The absorption of gas in a venturi device can be conveniently described in terms of conventional mass transfer principles. In the venturi absorber used for this process, flue gas containing SO_2 enters the converging section of the vessel and is accelerated towards the throat area, passing over surfaces which are irrigated by the absorbant slurry.

The moving gas creates a wave motion on the liquid surface until, at a critical velocity, the energy resulting from the frequency and amplitude of the waves exceeds the cohesive (surface tension, etc.) forces of the liquid. When this occurs, some portion of the wave is detached and dispersed into the gas stream.

The liquid, dispersed as droplets into the gas stream, provides the media for absorption. The equation for point efficiency,

$$(1 - E) = \frac{P_{SO_{2f}} - Pe}{P_{SO_{2i}} - Pe} = \exp\left[\frac{-Kg\ a\ Z}{G}\right] \qquad (1)$$

where
(E = Efficiency
(P = Partial Pressure of the Absorbed Gas
(Kg = Overall Mass Transfer Coefficient
(a = Area ft^2
(Z = Axial distance ft.
(G = Mass Velocity lb mole/hr. $ft.^2$

is useful in deriving relations for removal efficiency.

The surface area can be determined from the liquid to gas ratio in the absorber and the mean liquid drop size.

$$S = \frac{1.83 \times 10^6}{Do} \; \frac{Vl}{Vg} \qquad (2)$$

S = Specific Surface Area $ft.^2/ft.^3$
Vl = Volume of liquid $ft.^3$
Vg = Volume of gas $ft.^3$
Do = Mean drop diameter, μ

An estimate of Do can be obtained from the Nukiyama and Tanasawa equation (7)

$$Do = \frac{585\sqrt{\sigma}}{Ug\sqrt{\rho}} + 597 \left(\frac{\mu}{\sqrt{\sigma\rho}}\right)^{0.45} \left(1000\,\frac{Vl}{Vg}\right)^{1.5} \qquad (3)$$

Ug = Velocity of the gas, meters/sec.
ρ = liquid density, gm/cc
μ = liquid viscosity, poise
σ = liquid surface tension, dynes/cm

For the case of absorption with gas phase resistance controlling, it is possible to use an analogous form of equation 1 to correlate the data,

$$1 - E = \exp \left[-A \ \Delta P^B \right] \qquad (4)$$

ΔP = differential pressure (in. H_2O)
A & B are constants

For a particular installation (8) this has been used for a successful correlation as the vessel geometry and most operating conditions are set in the real system and dispersed area and gas flow are functions of ΔP.

For cases other than gas film controlling, an over-all mass transfer coefficient is defined as:

$$\frac{1}{Kga} = \frac{1}{kga} + \frac{\theta}{kla} + \frac{\theta}{ksa} + \frac{\theta}{kra} \qquad (5)$$

where the subscripts refer to the gas film, liquid film, solubility, and reaction resistances respectively.

The reactions involved are acid-base (fast) reactions, therefore, the final term in 5 can be considered zero. Recent investigations (9) have determined that the solids dissolution resistance is also zero.

In order to incorporate the contribution of liquid film resistance, we have correlated the data using the form

$$1 - E = \exp \left[\frac{-A \ \Delta P^B}{(10^{pH})^C \cdot (SO_2)^D} \right] \qquad (6)$$

SO_2 REMOVAL continued

This correlation is shown graphically in Fig. 4 , which presents the results obtained using the final form of the prediction equation.

$$F = 1 - \exp\left[\left(2.666(\Delta P)^{-1.014}(SO_{2I})^{-3.75 + .271 \ln SO_{2I}}(10)^{6 - .031\,pH}\right)^{-3}\right] \qquad (7)$$

F = Fraction SO_2 Removal

ΔP = Pressure Drop, inches H_2O

SO_{2I} = Inlet Concentration SO_2 (PPM)

This prediction equation has been developed from both the data obtained during the operations at Mystic Station in Boston, and from some subsequent additional data obtained during initial operations at an installation on PEPCO's coal fired boiler. This latter operation provided data for extension of the equation to higher pressure drops.

An estimate of the accuracy of the correlation for predicting SO_2 removal efficiency is given in the following table:

Source of Data	No. Of Points	Standard Deviation
Boston Edison	600	4.0 %
PEPCO	5	2.9 %
Boston Test Runs Used to Check Correlation	5	3.1 %

This correlation also illustrates the relatively small change in SO_2 removal efficiency (Fig. 4) experienced over wide turn down ratios of the plant in the normal operating range of the venturi absorber. An explanation of this potential to maintain high

SO_2 REMOVAL continued

efficiency over the ranges of power output of a cycling generating station, is the relative invariance of the surface area available for mass transfer over that range. Surface area calculations based on uniform drop size, and a constant liquid rate, show only a 33% reduction in surface area for a 4 to 1 turn down equivalent to operations between 40 MW and 150 MW.

CENTRIFUGE OPERATION

The centrifuge has operated satisfactorily for the greater part of the program. Problem areas have been wear of some parts of the centrifuge and four isolated periods when centrifuging did not separate solids at a rate sufficient for solids level control in the recycle slurry. It was demonstrated that proper selection of materials of construction would reduce the first problem to an acceptable level and that the second was related to a combination of chemical concentrations in the slurry which could be controlled.

Wear in the centrifuge was limited to the bowl plows, head plows, and the conveyor. No wear was observed in the centrifuge bowl itself. The conveyor was removed on three occasions to build up and re-hardface the flights. The plows and wear beads were also replaced. In the final repair, a stellite hard facing was applied to the flights. Later examination of the machine and comparison of wear rates after the stellite was applied indicated that this resulted in increasing the operating duration to one year before repair of the conveyor is necessary.

Wash-out connections were also added to the case and an internal wash pipe was installed to insure that solids deposits did not build up inside the unit.

Fig. 5 , shows the monthly average centrifuge performance from January thru June 1974 and is typical of the results obtained previously. In general, the centrifuge removes 40 to 60% of the solids in the stream fed to it. This level of separation has been satisfactory for control of recycle solids concentration in the desired 8 to 10% range.

CENTRIFUGE OPERATION continued

The low level of separation experienced in January had also occurred on three previous occasions. At these times the solids level in the recycle slurry rose uncontrollably forcing a system shut down. At first this was thought to have resulted from wear in the centrifuge (two of the centrifuge inspections were made as a result of these problems). Analyses of the data file revealed, however, a relationship to other chemical species in the system and this is shown in Fig. 6 .

While the factors affecting centrifuge performance are complex, it appears that the combination of increasing magnesium sulfate concentration and excess magnesia in the slurry result in an increase in viscosity coupled with hindered settling, which makes the separation more difficult.

Both of these concentrations can be controlled in the system. Actually, high magnesium sulfate levels had been induced during the problem periods by a practice of fuel switching to low sulfur fuel when a maintenance problem arose. This change in the SO_2/O_2 ratio resulted in a higher oxidation rate, more $MgSO_4$ in solution, and a worsening of the problem. This was easily remedied by eliminating the practice.

REGENERATION OF MAGNESIA

The principle operation in the regeneration plant is the calcination of the dryer product from the absorption system. This can be most simply described as a thermal decomposition:

$$MgSO_3 \xrightarrow[heat]{} MgO + SO_2$$

The rate of the decomposition is temperature dependent, and some decomposition has been observed at temperatures as low as 300°C. For the production of useful product in this program, the rotary calciner has been operated at mid kiln temperatures above 1000°F.

In addition to the simple decomposition of $MgSO_3$, the calcination step also serves the purpose of reducing the $MgSO_4$, a side product in the absorption reaction, which is also present in the feed.

This reaction can be represented by either of the following equations:

$$2MgSO_4 + C \longrightarrow 2MgO + 2SO_2 + CO_2$$

$$F_{1100°F} = -31 \text{ KCal}$$

$$MgSO_4 + C \longrightarrow MgO + SO_2 + CO$$

$$F_{1100°F} = -14 \text{ KCal}$$

REGENERATION OF MAGNESIA continued

Other reactions can also take place in the kiln environment:

$$1/2\ MgSO_4 \longrightarrow O_2 + 1/2\ MgS$$
$$MgSO_4 \longrightarrow MgO_2 + SO_2$$
$$2\ CO + SO_2 \longrightarrow 2\ CO_2 + S^\circ$$
$$1/2\ O_2 + SO_2 \longrightarrow SO_3$$

All of these reactions are both time and temperature dependent with the calciner equivalent to a multi-zone linear reactor. In the course of the program, in addition to the production of thousands of tons of acceptable regenerated MgO, upset conditions have resulted in the formation of high concentrations of SO_3 and at other times in the formation of elemental sulfur in the calcination step.

Attempts have been made to study these upset conditions in the laboratory, and thermal decomposition studies have been carried out there using infrared spectroscopic techniques to investigate the phenomena of sulfur formation by detection of its precursors appearance. These studies have not as yet yielded any specific information on the formation of elemental sulfur. However, they have yielded information indicating that the decomposition process for $MgSO_3$ obtained from the trihydrate form and from the hexahydrate form may be different.

Retention time in the calciner can be determined from the following equation:

$$\theta = \frac{0.19\ L}{N\ D\ S} \qquad (8)$$

where θ = time (min.)
L = kiln length (ft.)
N = Rotational Speed (RPM)
D = Dryer diameter
S = Slope (ft./ft.)

and for most operations undertaken during this project this time was approximately 1 hour. Because of the use of tube coolers on the calciner, an additional 1 hour was required before final discharge to the product conveyors.

An additional factor in the calcining operation is the formation of periclase, an unreactive form of MgO. This is generally accompanied by an increase in the density of the magnesia, and the following table shows the results of experiments to determine the effect of calcining temperature on specific gravity.

T°C	T°F	Specific Gravity
600	1112	2.94
710	1310	3.04
850	1562	3.22
1000	1832	3.39
1200	2192	3.48
1400	2552	3.52

The data resulting from the test program phase of this project was analyzed by regression methods to provide correlations for both the percent of $MgSO_4$ in the product and the bulk density of the product. These are given in the following equations and provide a means of determining the processing condition necessary for the production of an active magnesia. The effect on bulk density is shown graphically in Fig. 7 .

CALCINER OPERATIONS
CORRELATION FOR PREDICTION AND CONTROL OF BULK DENSITY OF REGENERATED MAGNESIA

$$BD = 169.2 + (T'*A) + (C*B) + 0.741\ (\%\ MgSO_4\ \text{in Feed}) - 0.744(\%\ MgSO_3\ \text{in Feed}) - 4.9\ (\%\ O_2\ \text{in Acid Gas}) - 0.4\ (\text{Feed Rate, LB./MIN.}) - 104\ (\text{Furnace Draft}) \qquad (9)$$

Where $T' = (1700 - {}^\circ F\ \text{Mid Kiln Temperature})^{1/2}$

$A = -0.891 + 0.166\ (C)$

$B = -28.4 + 3.44\ (C) + 71.2\ (\text{Furnace Draft}) + 1.95\ (\%\ O_2\ \text{in Acid Gas}) - 1.24\ (\%\ MgSO_4\ \text{in Feed})$

C = % Carbon in Feed

BD = Product Bulk Density, LB./FT.^{3} (Operation @ 1.82 RPM Add 5 to BD for 1.56 RPM)

Statistics: Standard Deviation = 7.2
Multiple Correlation Coefficient = 0.79
Confidence Level of F Ratio = 99.9% +
No. of Data Points = 456

CALCINER OPERATIONS
CORRELATION FOR PREDICTION AND CONTROL OF % $MgSO_4$ IN REGENERATED MAGNESIA

$$\%\ MgSO_4 = -90.2 + (T'*A)+(C*B) - 2.46\ (\%MgSO_4 \text{ in feed}) + 0.989(\%\ MgSO_3 \text{ in Feed}$$

$$+4.1\ (\%\ O_2 \text{ in Acid Gas}) + 0.28\ (\text{Feed Rate, Lb./Min.}) \qquad (10)$$

Where $T' = (1700 - {}^\circ F \text{ Mid Kiln Temperature})^{1/2}$

$A = -0.870 + 0.185\ (\%\ MgSO_4 \text{ in Feed})$

$B = 15.7 - 23.4\ (\text{Furnace Draft}) - 2.19\ (\%\ O_2 \text{ in Acid Gas})$
$-0.61\ (\%\ MgSO_4 \text{ in Feed})$

C = % Carbon in Feed

Statistics: Standard Deviation = 5.4
Multiple Correlation Coefficient = 0.77
Confidence Level of F Ratio = 99.9% +
No. of Data Points = 207

MgO LOSS AND REGENERATION CYCLES

A) Loss

In early operation of the system, losses of MgO were high. These losses resulted from the necessity for frequent clean outs, discarding both oversize material and any spilled solids, as well as loss to the stack, overflows, and absorber draining during the frequent shutdowns.

The installation, by June 1973, of the various lump crushers, as well as rerouting the dryer off gas to the absorber reduced this loss substantially in the following period but did not eliminate it. Spills were still discarded and the vessel was still drained on shut down.

Another contributing factor was the higher than design gas flow, which may have resulted in entrainment losses.

In the final period of operation, controls were imposed to eliminate many of the previously occurring gross losses, and during part of this period a careful measurement of system losses were made in order to identify these sources for future design improvements.

This loss history is shown graphically in Fig. 8, which accounts for the total system MgO loss by operating periods. The first, of about 1127 hours duration accounting for the greatest loss of 606 tons, corresponds to the pre-start, start-up, and shake-down period prior to June 1973.

The second period for test and development had a loss of 338 tons of MgO in 1630 hours of operation, and the last period for operational testing showed a loss of 151 tons in 1350 hours of operation.

MgO LOSS AND REGENERATION CYCLES continued

A) Loss continued

In the final period starting in March 1974, gas flow to the absorber was maintained at the design rate. In addition, the system was run as a closed loop with no vessel drainage, returning the small spills back to the process. Measurements were made at the following 14 loss points at Boston for a continuous operations period and the silos were emptied and the contents weighed before and after the run.

Potential Sources of MgO Loss at Mystic Station

1) Stack
2) Centrifuge Washing
3) Centrifuge Case Leaks
4) Pump Packing Gland Leaks
5) Absorber Overflow
6) MgO Slurry Tank Blow-Down
7) MgO Slurry Tank Overflow
8) Centrate Tank Overflow
9) Solids Loss at Dryer Feed End
10) Dust Loss at Dryer I.D. Fan
11) Dust Loss at Expansion Joints
12) Spillage at MgO Feeder
13) Spillage in $MgSO_3$ Belt Gallery
14) Spillage at Truck Loading Point

The tests, conducted over 13 days, in which 336,470 lbs. of regenerated material were fed (an additional 2,504 lbs of MgO added with the fuel oil was also accounted for), showed a loss of 0.37 tons/operating day at the absorber system distributed as follows:

Loss to Stack	0.13	Ton/Day
Absorber Overflow	0.14	"
Misc. Measured Loss	0.07	"
Unmeasured Loss (By Difference)	0.03	"
	0.37	"

A) Loss continued

With an average MgO consumption of 10.61 tons/day during the period, this amounts to a 3.5% loss as compared to a 5% design.

The greatest losses were found to occur at the regeneration plant. Here 1.5 tons/day of equivalent MgO is lost from the neutralizer system overflow and another 0.5 tons per day is scalped off, for future reclamation, before being pulverized.

Both of these losses would be virtually eliminated in a full size regeneration plant.

B) Regeneration Cycles

Fig. 8 can also be used to evaluate the number of regenerations of magnesia in the various operational periods.

In the start-up and shake-down period, losses were 606 tons of MgO, with 559 tons of regenerated MgO recycled to the Mystic #6 System. This rate limited the number of recycles from 2 to 3 before the material was lost from the system.

During the test and development period, 1717 tons of regenerated MgO were returned to the system, while 338 tons of MgO equivalent were lost. This corresponds to 5.1 cycles for the magnesia before it is lost from the system.

During the final period, 151 tons of magnesia was lost, while 875 tons of regenerated alkali was shipped back to Boston. This would correspond to 5.8 cycles; however, during this same period there was an inventory build-up with 80 tons of equivalent MgO

B) Regeneration Cycles

inventory at the beginning, and 214 tons remaining at the close of the program. The actual number of cycles reached a maximum of 5 at the beginning of May.

The negligible effect of regeneration of magnesia on the process is also seen in the monthly average analysis of excess MgO in the centrifuge cake, which only increased from 1.7% in March to 3.6% in April.

CONCLUSIONS

Problems encountered by previous workers attempting to use magnesia as the chemical agent for flue gas desulfurization have been overcome in the Chemico-Basic Process. Operation of the prototype plant over the two year period covered by this series of reports has demonstrated that:

1) Slurry solids separation has been maintained. Use of a centrifugal separator and control of the chemical components in the slurry, which influence the seperational methods, both contribute to the solution of this problem area.
2) Magnesium sulfate concentration can be controlled and the magnesium sulfate formed can be regenerated. Controlled addition of carbon to alter the calciner atmosphere and modify the reducing conditions has proven successful in eliminating the problem of eventual complete conversion of the alkali to $MgSO_4$.
3) Plugging and scaling of the absorption equipment has not been a problem. High circulation rates, controlled slurry composition, high crystallization nucleii concentration, and limited residence time are all contributers to the solution of this problem area.

Several new problems were encountered and overcome during operation of the prototype system, and their description has been reported in this paper and references 5, 6. It now would appear that incorporation of the developed modifications into the next plants, coupled with a mechanical redesign to incorporate simpler and more robust material handling equipment and the use of rubber lined slurry pipe, pumps, and valves, would result in a reliable system for flue gas desulfurization.

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TABLE 1

SO_2 REMOVAL - TEST RESULTS

TEST NO.	BOILER LOAD: MW	INLET GAS RATE: ACFM	SO_2 IN PPM - VOL.	SO_2 OUT PPM - VOL.	% SO_2 REMOVAL	SO_2 OUT $LB/10^6$ BTU
1	146	446,953	926.1	71.1	92.3	0.125
2	144	486,991	1004.5	89.0	91.1	0.199
3	151	658,207	983.9	63.3	93.6	0.201
4	148	503,233	833.3	86.6	89.6	0.243

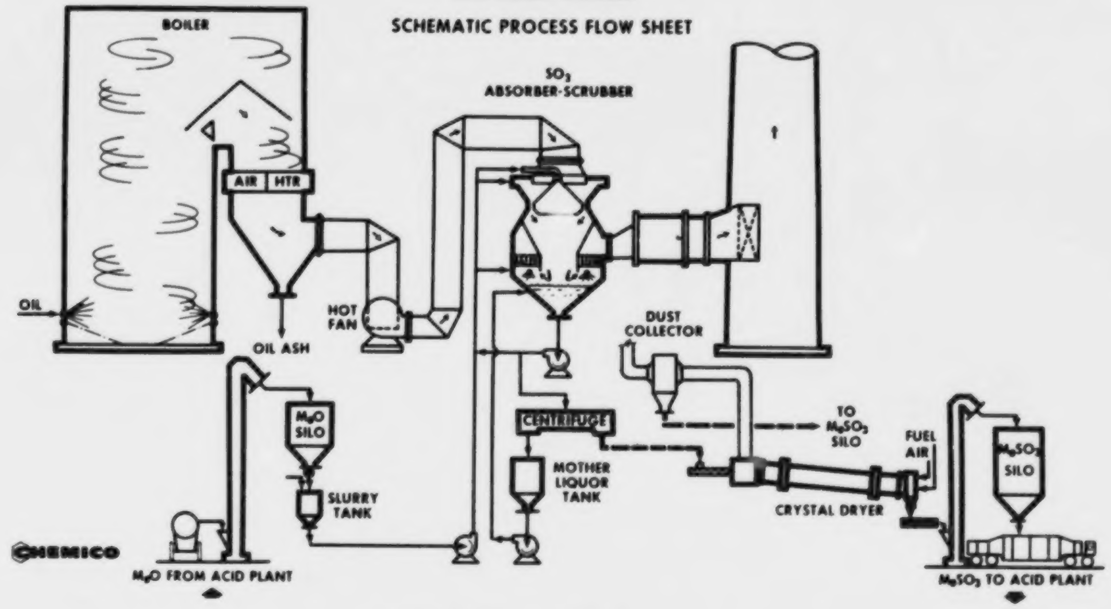
TABLE 2

PARTICULATE REMOVAL - TEST RESULTS

TEST NO.	BOILER LOAD: MW	INLET GAS RATE: ACFM	PARTICULATES: LB/HR		% REMOVAL	PARTICULATES LB/10^6 BTU
			IN	OUT		
1	146	446,953	380	116	69.5	0.072
2	144	486,991	232	115	50.4	0.084
	151	658,207	399	150	62.4	0.111
4	148	503,233	151	82	45.7	0.068

MgO ADDITIVE SCRUBBER SYSTEM FOR SO_2 RECOVERY OIL FIRED BOILER

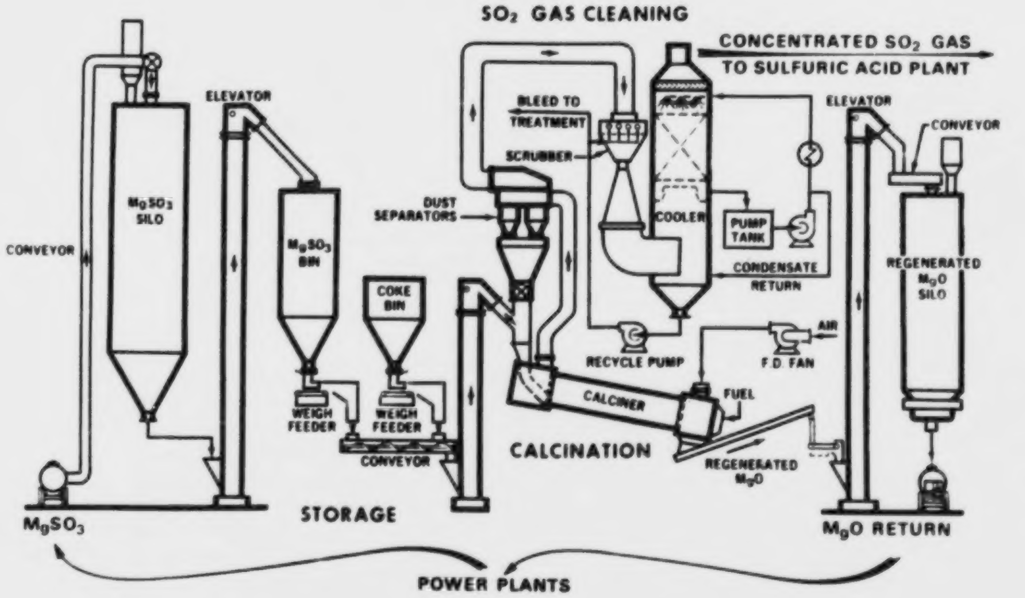
SCHEMATIC PROCESS FLOW SHEET

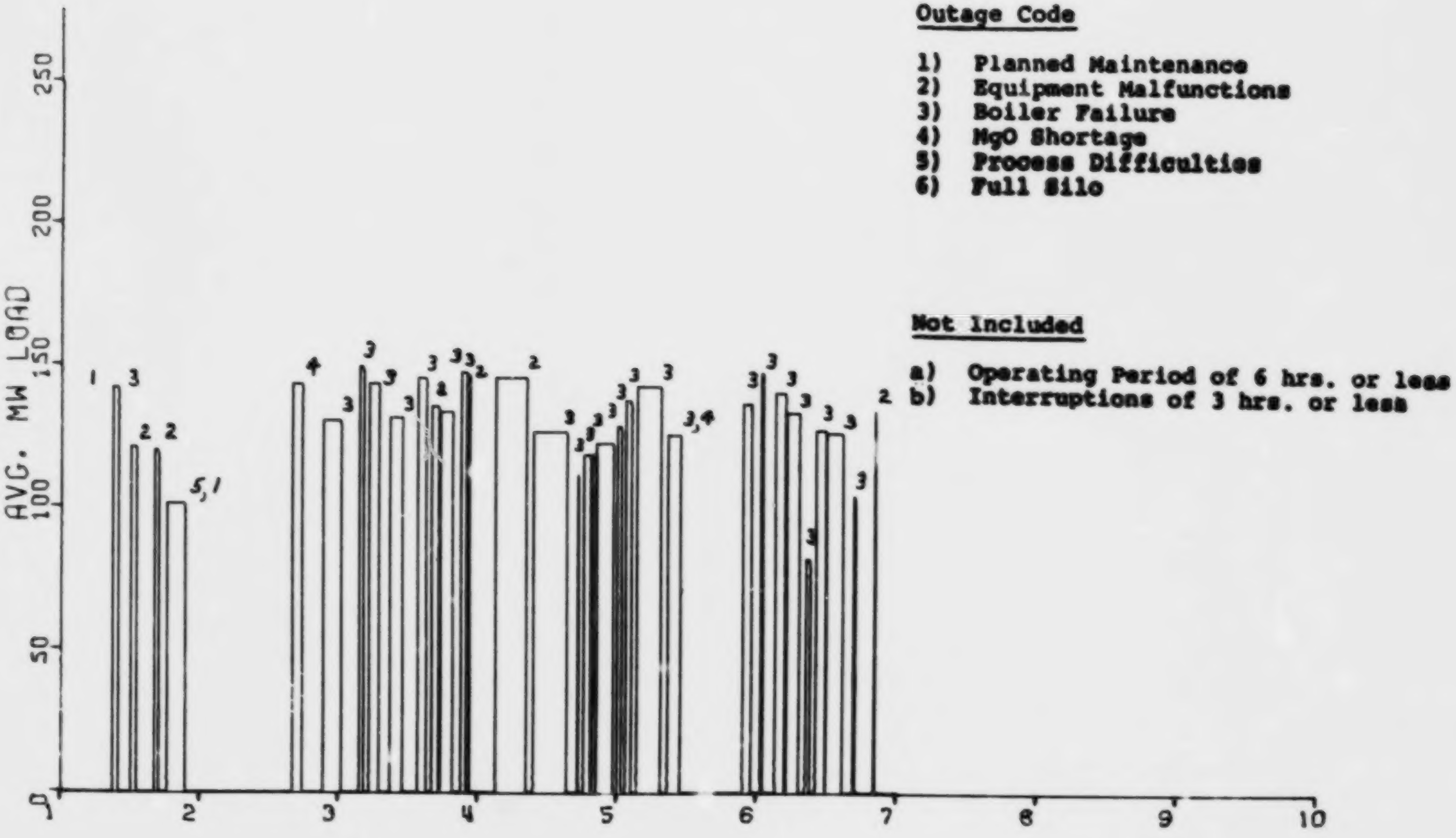

BOILER
SO_2 ABSORBER-SCRUBBER
AIR HTR
OIL
OIL ASH
HOT FAN
DUST COLLECTOR
TO $MgSO_3$ SILO
FUEL
AIR
$MgSO_3$ SILO
MgO SILO
CENTRIFUGE
SLURRY TANK
MOTHER LIQUOR TANK
CRYSTAL DRYER
CHEMICO
MgO FROM ACID PLANT
$MgSO_3$ TO ACID PLANT

REGENERATION SYSTEM

MgO RECYCLE PROCESS, FOR PRODUCTION OF 98% SULFURIC ACID

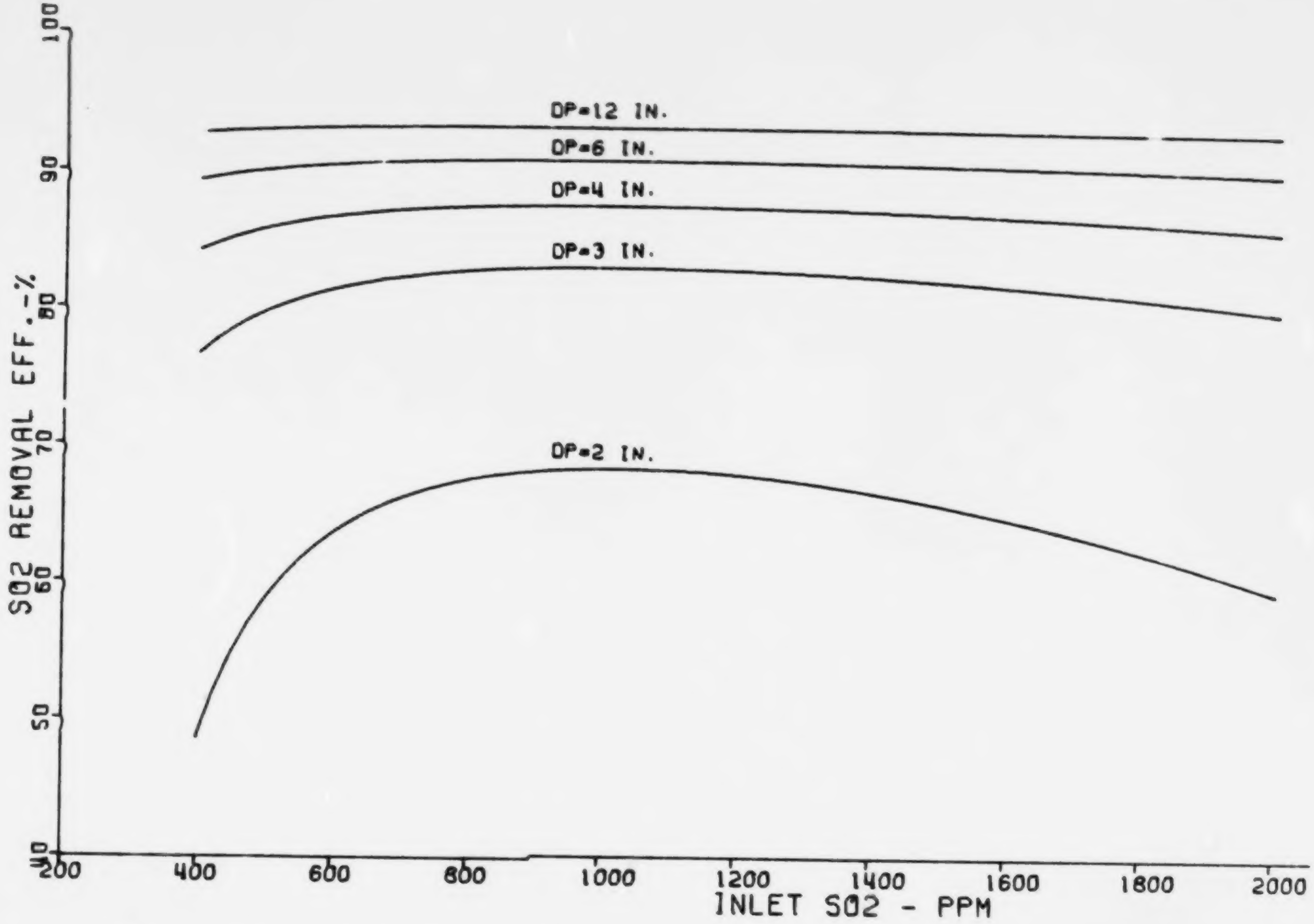
SCHEMATIC PROCESS FLOW SHEET


SO_2 GAS CLEANING
CONCENTRATED SO_2 GAS TO SULFURIC ACID PLANT
BLEED TO TREATMENT
SCRUBBER
ELEVATOR
ELEVATOR
CONVEYOR
CONVEYOR
$MgSO_3$ SILO
$MgSO_3$ BIN
COKE BIN
DUST SEPARATORS
COOLER
PUMP TANK
CONDENSATE RETURN
REGENERATED MgO SILO
RECYCLE PUMP
AIR
F.D. FAN
FUEL
CALCINER
WEIGH FEEDER
WEIGH FEEDER
CONVEYOR
CALCINATION
REGENERATED MgO
STORAGE
$MgSO_3$
MgO RETURN
POWER PLANTS



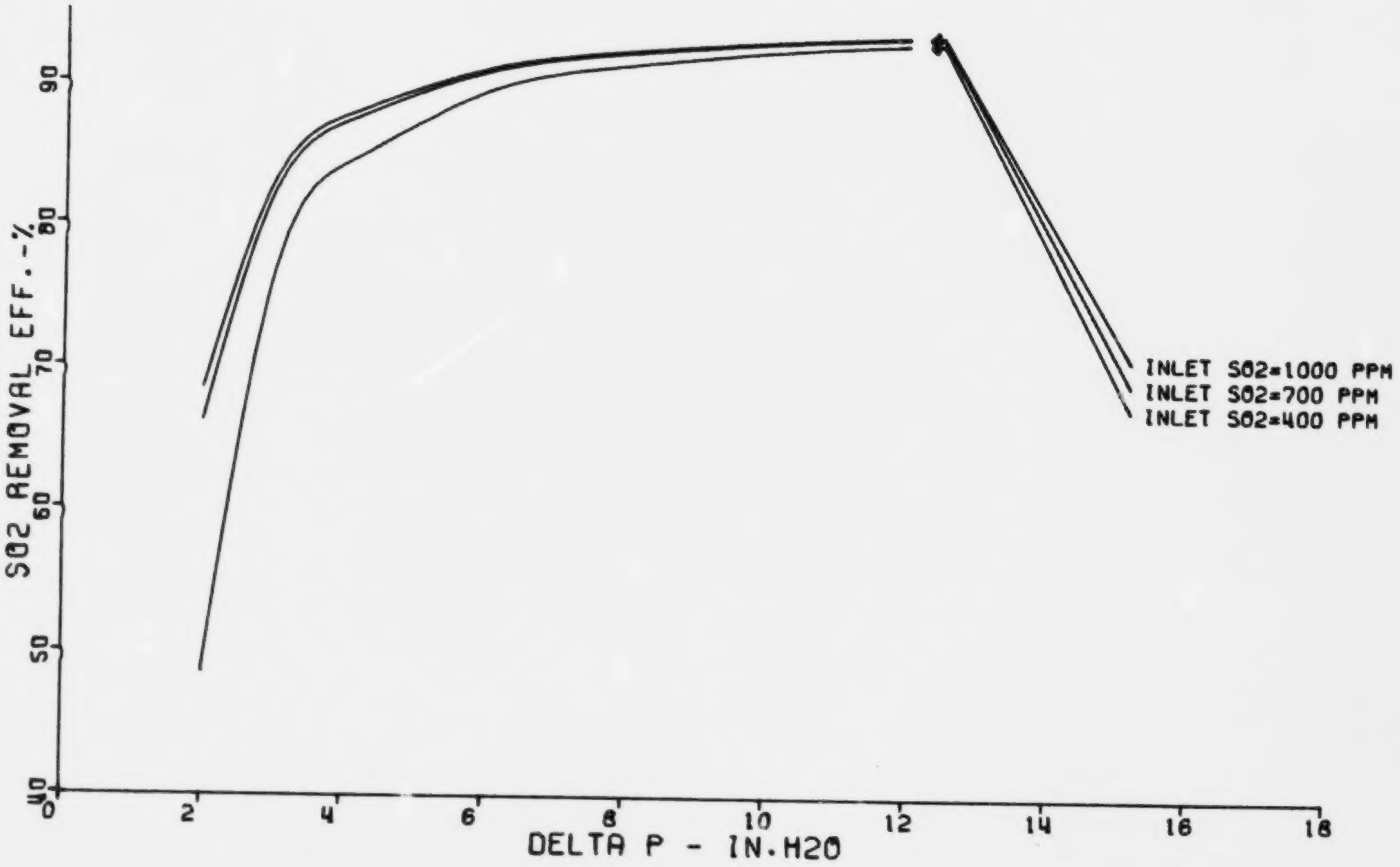
BOSTON ED. OPERATIONS JAN.-JUNE 1974

Fig. 2



SO2 REMOVAL EFFICIENCY
EFFECT OF DELTA P AND INLET SO2 CONC.

Fig. 3



SO2 REMOVAL EFFICIENCY
EFFECT OF DELTA P AND INLET SO2 CONC.

Fig. 4

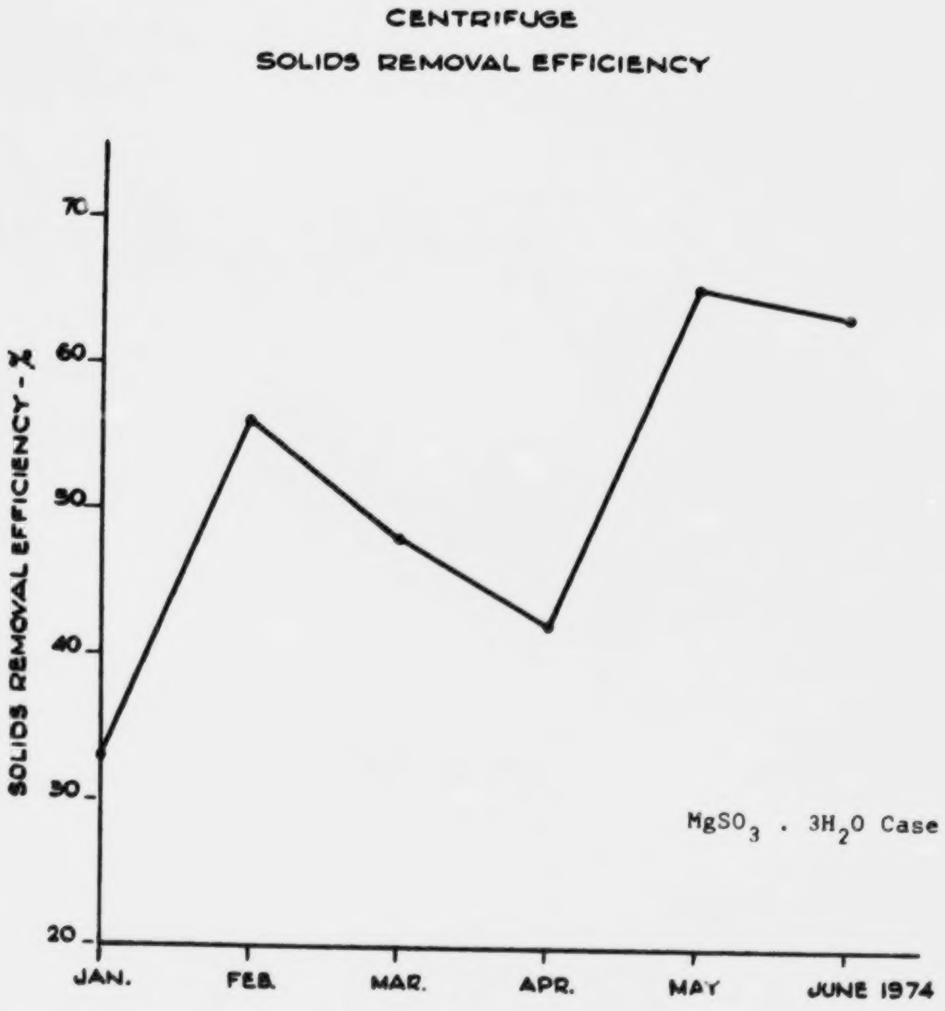
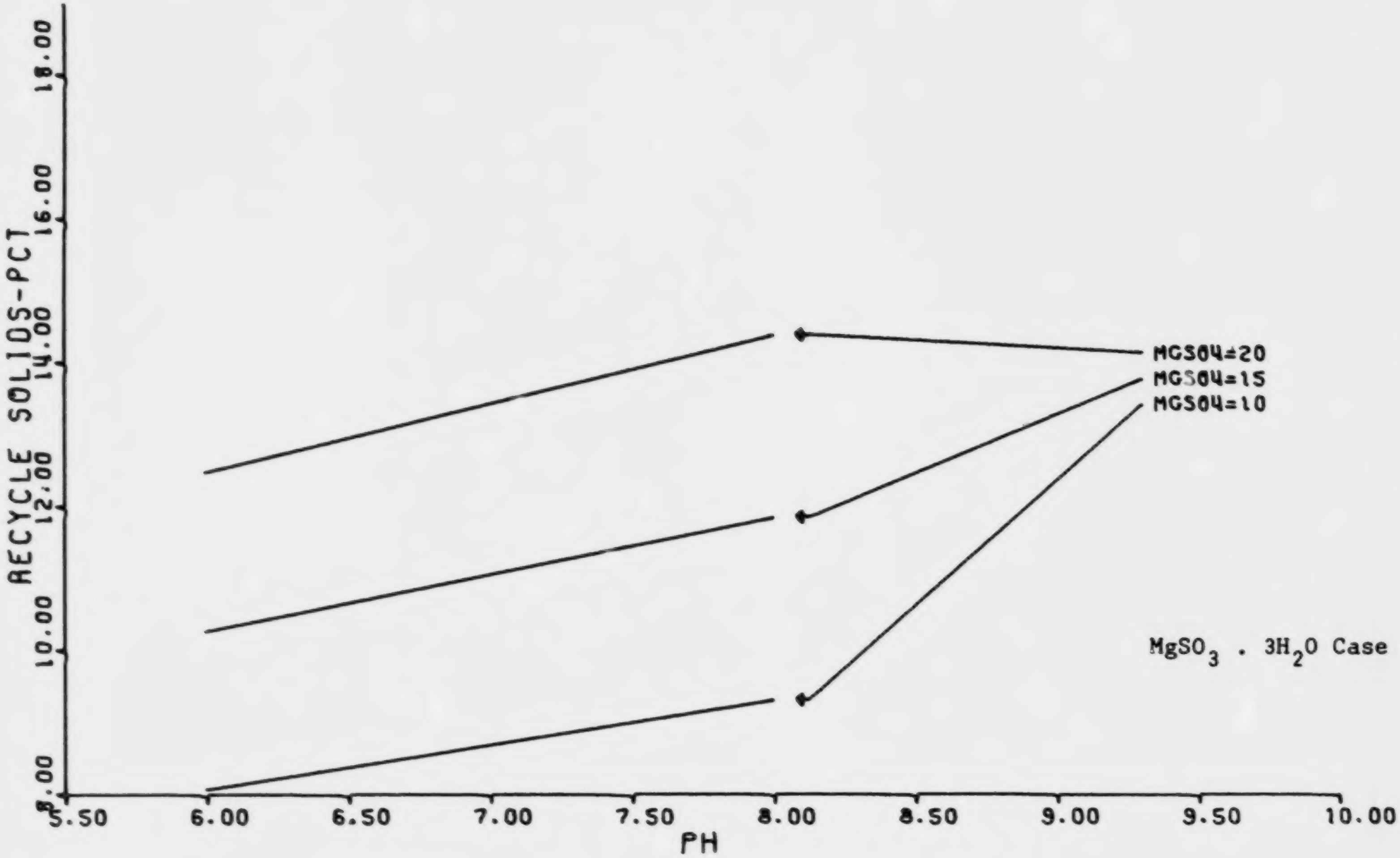
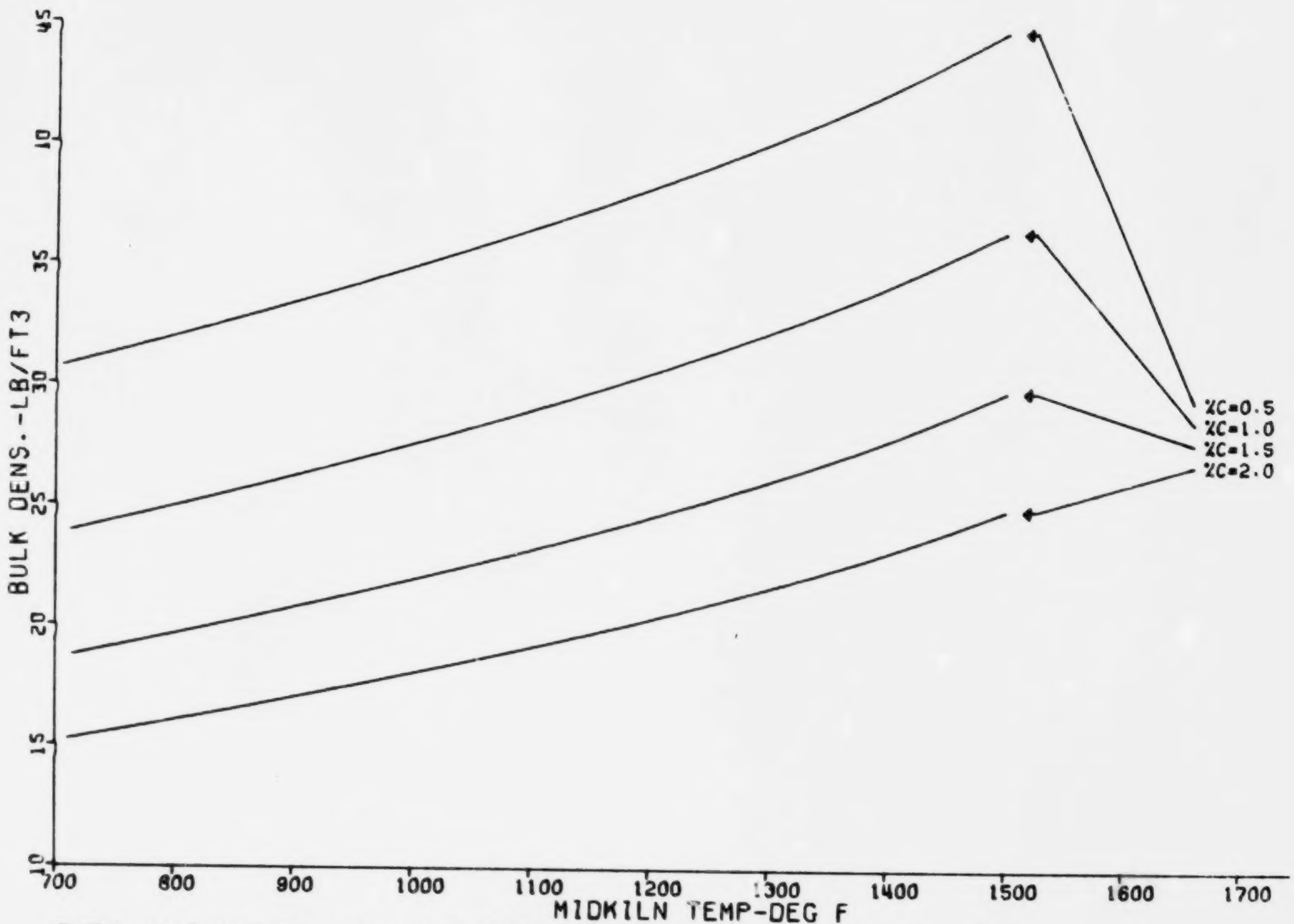

CENTRIFUGE
SOLIDS REMOVAL EFFICIENCY
SOLIDS REMOVAL EFFICIENCY - %
70
60
50
40
30
20
JAN.
FEB.
MAR.
APR.
MAY
JUNE 1974
$MgSO_3 \cdot 3H_2O$ Case

Fig. 5



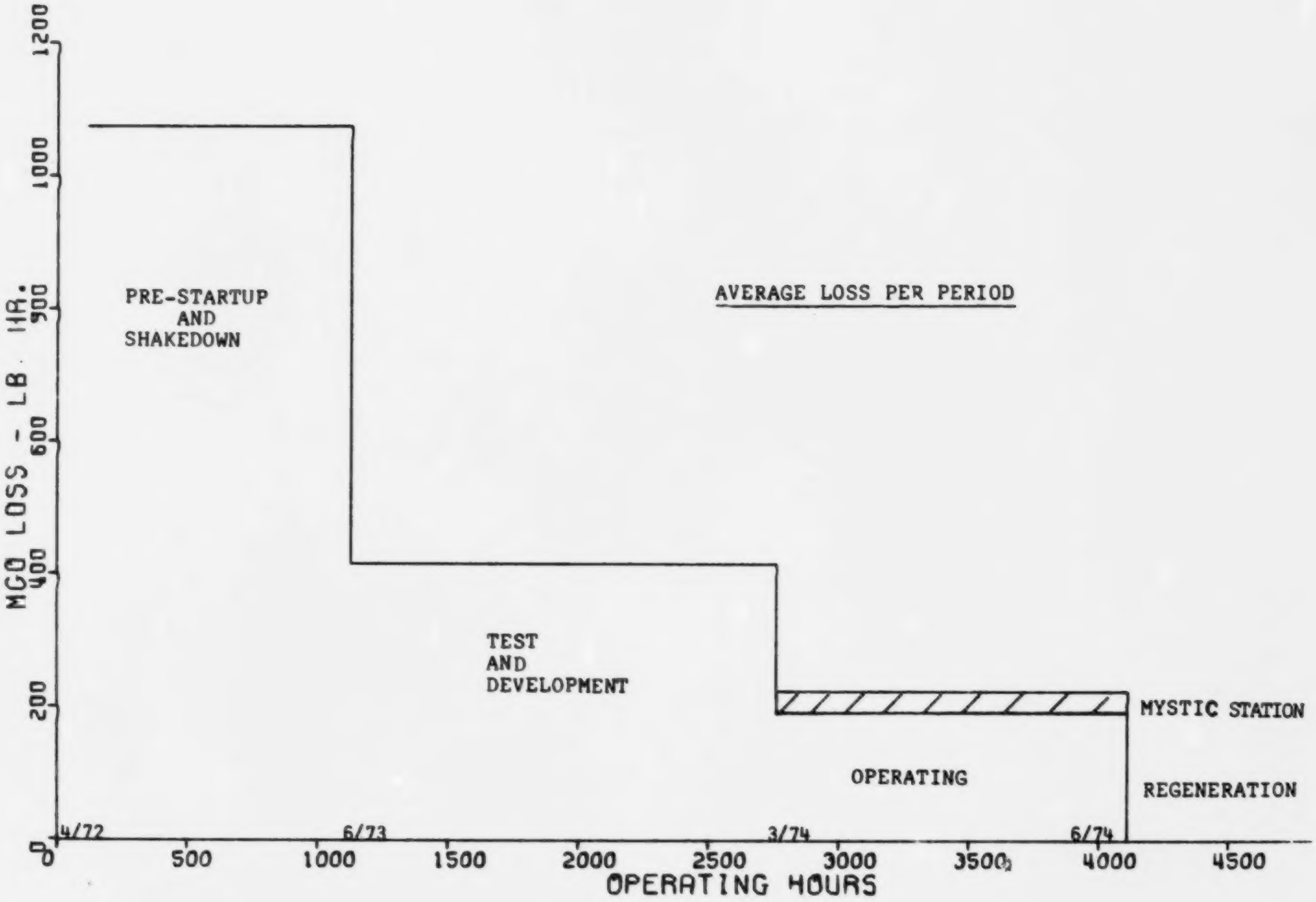
EFFECT OF SYSTEM PH AND MGSO4 LEVEL
ON RECY.SOLIDS CONTENT -DATA TO 3/12/74

Fig. 6



CALCINER OPERATION - EFFECT OF
MIDKILN TEMP. & %C. ON BULK DENSITY

Fig. 7



PROCESS MGO CONSUMPTION
BY OPERATING PERIODS

Fig. 8

ASSESSMENT OF PROTOTYPE OPERATION AND FUTURE EXPANSION STUDY - MAGNESIA SCRUBBING MYSTIC GENERATING STATION

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ASSESSMENT OF PROTOTYPE OPERATION AND FUTURE EXPANSION STUDY - MAGNESIA SCRUBBING MYSTIC GENERATING STATION

Christopher P. Quigley
James A. Burns

INTRODUCTION

Boston Edison Company, from April 1972 through June 1974, operated and maintained a prototype magnesium oxide scrubbing system installed on its Mystic Station Unit #6, a 156 MW oil-fired unit, in Everett, Mass. The magnesium oxide system, including the facilities for regeneration of the MgO located at an Essex Chemical Company acid plant in Rumford, Rhode Island, are described in detail in a separate paper presented by Chemico at this session and in prior papers. The intent of this presentation is to discuss specific aspects of scrubber operation and maintenance including availability and cost of the prototype system at Mystic Station. Also included are details of a conceptual expansion of scrubbing at Mystic Station along with a discussion of other factors now being studied which will affect Boston Edison's eventual decision on the installation of additional scrubbing capacity.

SCRUBBER OPERATION

Early in the planning stages of the scrubber project only a normal type and volume of operational activity was anticipated due to the relatively small amount of equipment in a compact area. On this basis, 1 auxiliary operator per shift with part time supervision was assigned. Upon startup of the system, operational problems developed over a period of time which made it necessary to assign 2 auxiliary operators and full time supervision on each shift with cleanup crews assigned as required.

Some of the early operational problems requiring additional manpower included inoperable flue gas dampers, inability to keep rotary dryer burner operating along with cleanup associated with hardened deposits, dust carryover, and formation of agglomerates in the rotary dryer, unreliable Ph instrumentation which forced constant manual sampling and analysis, insufficient capacity of dryer feed screw, and general cleanup of dust and slurry on equipment and ground.

As equipment modifications and additions were made to improve scrubber operation a more complex system resulted. Also, with an increasing knowledge of existing equipment limitations and complexities, a requirement for anticipating and adjusting for system excursions evolved. Under these circumstances it became necessary to consider a more technically oriented operator. In late 1973, one Central Control Operator and one Supervisor on each shift were assigned to the project replacing the less experienced auxiliary operators. An additional CCO and cleanup crews were available on any shift as required. This reassignment of manpower and the extensive maintenance program on pumps and centrifuge in December 1973 and January 1974 was in large measure responsible for the generally more successful operation experienced through the end of the program.

SCRUBBER MAINTENANCE

Scrubber maintenance throughout most of the test program was excessive both in terms of manpower requirements and spare parts. This was especially true when considering the very low quantity of scrubber operating hours attained during this period. This condition existed until the Spring of 1974 when most of the major problems were resolved.

Because we were making concentrated efforts to demonstrate continuous scrubber operation we could not in a short test program take the time to make major changes. This resulted in recurring breakdowns of equipment which was not really suited for the application. While many examples could be cited to illustrate the problems, three areas will be discussed.

Dryer Feed Screw Conveyor

The dryer feed screw conveyor carrying wet cake from the centrifuge to the rotary dryer caused repeated scrubber outages. Initially, dryer dust captured in the mechanical collector on the dryer off-gas was reinjected into the wet cake just prior to passage into the dryer. Premature drying resulted in the buildup of hardened deposits in the conveyor, both inside and outside the rotary dryer. These deposits caused overloads, damaged gear boxes and motors, and resulted in erosion and twisting of the conveyor housing.

Changes to the conveyor housing, and transport of the dryer dust to storage rather than to the wet cake conveyor eliminated some of the problems but buildups in the conveyor within the rotary dryer remained a problem.

Centrifuge

Centrifuge problems basically involved buildup of hardened air-dried slurry within the centrifuge. Maintenance work included a range of tasks from repetitious replacement of shear pins (pins provide mechanical overload protection to internals in the event of binding), to the complete dismantling of the centrifuge for cleaning and repair to worn solids conveyor. Assignment of 3 or 4 maintenance men for dismantling and cleaning, shipment of internal conveyor to manufacturers shop for rebuilding and hardface replacement, and reinstallation of centrifuge was required on several occasions. Each of these maintenance experiences required approximately 1 week.

Erosion/Corrosion of Pumps, Valves, etc.

The major area of maintenance committment in terms of both manpower and spare parts was due to erosion/corrosion of slurry pumps, large isolation valves and expansion joints around recycle pumps, and various piping. Original design had included cast iron slurry pumps, carbon steel unlined piping, carbon steel valves with rubber lined plugs, and rubber expansion joints around the large recycle pumps. Because of the limited time available in the test program very few attempts at optimizing equipment could be made. Stainless steel impellers, for example were installed with little or no improvement observed. As the test program progressed we considered ourselves fortunate to obtain the necessary cast iron parts to keep pumps running. Erosion/corrosion in the 6 - 18 inch valves on the discharge and suction of the main recycle pumps eventually prevented isolation of the pumps for maintenance. Six new valves were installed in the same materials, that is, carbon steel bodies with rubber-lined plugs. New valves with the entire body rubber-lined could not be made available on time. Several of the large rubber expansion joints installed on the recycle pumps showed erosion and splitting of the rubber and were replaced. Maintenance welding of piping especially at changes of flow direction in small piping was constantly required. Erosion/corrosion of piping in the tangential spray header piping to the absorber was a particular problem.

From startup in April 1972 to February 1974 the requirement for maintenance was continuous. Assignment of manpower varied from 1 man for the smallest job to 12 men during the heaviest periods of maintenance for overhaul. After the major maintenance program on pumps, valves, centrifuge, etc. was completed in February 1974 maintenance requirements fell off considerably through the end of the program (June 1974) as would be expected with the increase in scrubber operating hours in this period.

SCRUBBER AVAILABILITY

From startup in April, 1972 through May, 1973 the scrubber operated with a very low availability of 17% of Unit #6 operating hours. Availability is defined as the hours of scrubber operation divided by the hours of boiler operation. Through June and July 1973 scrubber availability improved to 68 and 61% respectively. During the remainder of 1973 availability fell off due to the heavy erosion-corrosion experienced in pumps and centrifuge. Maintenance work was completed in February, 1974 with all efforts directed to improving the status of equipment for the final stages of the 2 year test program. Scrubber availability improved from March through June 1974 as evidenced by the following data:

	Unit #6 Operated	Scrubber Operated	Availability
June 1973	592	402	68%
July	575	351	61%
August	Unit #6 and scrubber out for overhaul		
September	637	243	38%
October	627	377	60%

	Unit #6 Operated	Scrubber Operated	Availability
November	629	162	26%
December	658	86	13%
January 1974	555	152	28%
February	541	138	25%
March	408	353	87%
April	585	471	81%
May	488	280	57%
June	359	288	80%
Total	6654	3303	

Scrubber availability from June 1973 through June 1974 was 50%.

The longest continuous periods of scrubber operation occurred for approximately 7 days on 3 separate occasions. Two of these continuous runs were in April, 1974. From March, 1974 through the end of the program in June, 1974 the inability to demonstrate longer runs was due primarily to Unit #6 boiler problems which were not related to scrubber operation.

COST REVIEW - SCRUBBER PROTOTYPE

The capital investment in scrubber plant at Mystic Station which includes the centrifuge and drying facilities amounts to $3,635,000. This figure does not include $1,382,447 for general and administrative expenses and allowance for funds used during construction.

Scrubber operation and maintenance costs at Mystic Station over the 2 year test program are shown as follows:

Operating Labor	$390,000
Mechanical & Electrical Maintenance including Spare Parts	380,000
Extraordinary Cleanup Maintenance	65,000
Instrument Maintenance	32,000
Operating Materials	132,000
Total	$999,000

The cost to operate and maintain this prototype system was excessive due to the unusual operational and maintenance problems experienced. It is not advisable we feel, to apply the above cost during a 2 year test program to a future design. Experience through a 2 year program has, however, enabled us to prepare a reasonably accurate assessment of future capital, operating, and maintenance cost.

Estimates of these costs for scrubbers installed on Mystic Station Units with 1050 MW of electrical capacity are presented later in this paper.

MYSTIC STATION PROTOTYPE SUMMARY

Boston Edison has appraised the scrubber project at Mystic Station as reasonably successful under the circumstances of an erratic test program due to very intermittent operation. We prefer, however, to continue to detail areas of success and failure in order for others to individually assess the project.

Areas of Success

1. SO_2 removal efficiency obtained throughout the program was generally in excess of 80%. Independent performance testing using EPA test methods during late February and early March 1974

showed SO_2 removal efficiencies averaging 91.1% with the use of regenerated MgO.

2. Minor scaling in the absorber was observed but never interfered with operation. No plugging of mist eliminators occurred at any time. Once past early problems of slaking the regenerated MgO which caused plugging in MgO slurry lines, no plugging occurred in the pumps and piping systems.

3. Late in the scrubber test program tube failures in Unit #6 boiler caused several scrubber shutdowns. The scrubber system repeatedly showed its ability to cycle with the boiler by returning to service immediately after boiler repairs.

4. The project resulted in the production and sale of approximately 5000 tons of a commercial grade of sulfuric acid.

5. As a research prototype the major goal was to demonstrate the chemical reactions on a large scale and uncover and solve technical problems introduced in the scale up from pilot plant operation. Although the 2 year test program was conducted under very erratic conditions it was clear that basic concepts of SO_2 removal, MgO regeneration, and production of sulfuric acid were feasible.

Areas of Failure

1. Poor availability over a 2 year test program.

2. MgO losses throughout the system (scrubber and calciner) were excessive and amounted to approximately 10% at the end of the program.

3. The ability of the regenerated MgO to be recycled continuously while maintaining its capability to react with SO_2 in a tight system with minimal MgO makeup was not demonstrated. In addition, with high MgO system losses an evaluation of buildup of ash, vanadium, etc. was inconclusive.

EXPANSION STUDIES

Conceptual Arrangement

Expansion of scrubbing at Mystic Station using the MgO process has been studied in detail. In the expanded system the flue gases of Unit Nos. 4, 5, 6 and 7 would be scrubbed and a central calciner facility would be located on site to process the magnesium salts produced. The SO_2 gas would be fed to a sulfuric acid plant on an "across the fence" basis.

The system was sized to scrub 1050 MW of oil fired boilers burning a residual fuel of up to 3.5% sulfur content. Operating costs were evaluated for the system on the basis of firing 9,738,000 barrels per year of residual fuel oil with a 2.5% average sulfur content (plant load factor of 71.2%).

Figure 1 shows a simplified process flow diagram. The scrubbers and slurry recirculating pump systems would be located in the vicinity of the individual unit stacks similarly arranged to the existing Unit #6 system. Unit Nos. 4 and 5, each rated at 150 MW, will be virtual duplicates of the Unit #6 scrubber arrangement. Unit #7, a new 600 MW unit, would be equipped with two scrubbers.

The expanded scrubbing system would supply magnesium sulfite slurry to a central regeneration plant located either on the property or on property adjacent to the power plant site.

The regeneration plant would centrifuge, dry, and store the magnesium sulfite received from the boiler plant. From storage, the sulfite salts would be processed through a calciner, driving off the SO_2 gas to an adjacent acid plant and regenerating the MgO for reuse in the scrubbers. MgO would be slurried with water at the regeneration plant and pumped back to the scrubbers.

Built into the process would be points for buffering against equipment breakdowns, planned equipment shutdowns and variances in equipment process loadings. Each scrubber would be equipped with a by-pass duct to enable the boiler to continue to operate in the event scrubber shutdown is required. The $MgSO_3$ silos and the MgO silo would be sized to provide buffer storage. This excess storage would provide for the varying flow of materials to and from the power plant while supplying an essentially base loaded acid plant. In addition, this storage permits the continuation of scrubbing operations during a normal acid plant annual overhaul. The calciner and acid plant would be sized to provide "catch-up" calcination ability.

This arrangement differs from the Unit 6 experience in that no "off-site" transportation is involved. Further, the centrifuging, drying, dry material handling and MgO slurry preparation steps are divorced from the power plant area and centralized with the calciner operation. This would enable us to adequately control material losses. The handling of dry dusty materials is localized and minimized. The losses from cleaning dryer and calciner off gases could be virtually eliminated by using the effluent from scrubbers on these off gases as makeup to the MgO slurry system located in the same area.

System control would be split between the two locations. At the boiler plant, the operators would control flue gas fan and damper systems and the feed of MgO and bleed of $MgSO_3$ at the scrubbers. Chemical analysis work relative to scrubber operation would also be performed by these operators. The process plant operators would control the more complicated chemical operation of calcination as well as the centrifuging, drying, material handling, storage and batching operations of the process. The process plant would be staffed by operators and maintenance personnel trained in the skills required in a modern chemical process plant - skills not normally developed in the power industry.

SCRUBBER PLANT DETAILS

Design Flue Gas Conditions

The system would be sized for the following flue gas conditions:

	Boiler Nos. 4, 5, 6 (Each)	Boiler No. 7
Flow - ACFM	550,000	1,910,000
Temperature - °F	280	381
SO_2 Inlet - ppm	1091	1532
SO_2 Outlet - ppm	109	153
Inlet-Particulate gr/SCF	*	0.156
Outlet-Particulate gr/SCF	*	0.0363
Pressure Drop	8" WC	19" WC

* To be determined from Unit #6 testing

Utility Requirements

Utility requirements at the scrubber plant are estimated as follows:

Power: 13,800 kW at 4160 kV

230 kW at 480V

Water: 960 gpm

Steam: 500 #/hr. max. at 50 psig

Mother Liquor (From Regeneration Plant): 2350 gpm

MgO Slurry (From Regeneration Plant): 262 gpm

Major Components

The following lists the major components to be provided at the scrubber plant:

Item	Unit #4	Unit #5	Unit #6	Unit #7
Fixed throat venturi absorber	1	1	1 (exist.)	2
Scrubber Recycle Pumps	2	2	3 (exist.)	4
Sump Pumps	2	2	2	2
Induced Draft Booster Fans	2	2	2 (exist.)	2
Instrument & Control Boards	1	1	1	1
Scrubber Holding Tank	1 - Common to all units			
Instrument Air System	1 - " " " "			
4 kV Switchgear	1 - " " " "			
480 V Switchgear	1 - " " " "			
300 kVA Transformer	1 - " " " "			
33' x 70' Control Bldg.	1 - " " " "			

REGENERATION PLANT DETAILS

Production Capability

Operating logistics have been estimated based upon power plant generation of 1050 MW at an average annual plant load factor of

71.2% burning a 2.5% sulfur oil with a 90% SO_2 removal efficiency. On this basis, the plant would produce approximately 72,000 Ton/year of SO_2 supplying the feed stock for a 350 Ton per day H_2SO_4 plant.

Utility Requirements

Utility requirements at the regeneration plant are estimated as follows:

Power: 2800 kW at 4160 kV
1360 kW at 480 V

Water: 392 gpm

Steam: 29,765 #/hr. at 50 psig

#6 Fuel Oil: 28,840 gal./day

Coke: 3.3 tons/day

MgO Makeup: 7.7 tons/day

Major Components

Major equipment provided at the regeneration plant consists of:

Item	Quantity
Centrifuges	10
Rotary Dryers	2
Dryer Scrubber	1
Calciner	1
Calciner Scrubber	1
Weak Acid Coolers	2
Cooling Tower	1
Mechanical Dust Collectors	12
Miscellaneous Tanks	12
Miscellaneous Conveyors	14
Fans and Blowers	12
Process Pumps	22

Major Components (continued)

Item	Quantity
Fuel Oil System including storage & 2 pump and htr. sets	1
Instrument Air System	1
Instruments & Control Boards	
4 kV Swgr. Units	2
480 V Mtr. Control Centers	2
1000 kVA 4 kV/480 V Transformers	2
Centrifuge Building (48' x 75' x 55' high)	1
Office/Warehouse Bldg. (40' x 80' x 12' high)	1
Calciner Bldg. (35' x 60' x 48' high)	1
$MgSO_3$ Storage Silo (40' dia. x 130' high - reinf. conc.)	2
MgO Storage Silo (40' dia. x 130' high - reinf. conc.)	1

Cost Summary

Capital cost for such a conceptual plant is currently estimated at $51/kW. This cost does not include the cost of a sulfuric acid plant which would be owned and operated by others. Total capital and operating costs for the scrubber/regeneration facility based on the plant loading used in this study are estimated to be 2.44 mils/kWh.

Assessment

The Boston Edison Company believes we have demonstrated the technical feasibility of magnesia scrubbing. However, we were not able to demonstrate a long sustained run commensurate with power plant needs. We are reasonably certain we can build a second generation large scale system based on the knowledge gained with the Unit #6 prototype. Some risks would be involved. For example, we believe the erosion/corrosion problems associated with pumps and piping would be solved by rubber coating critical components. We have, however, not had the opportunity to test this modification. The absorber size for Unit #7 will escalate to 900,000 acfm from the 450,000 acfm design of Unit #6. Although there is some risk in this extrapolation, it certainly does not match the original risk in extrapolating from the 1500 acfm pilot to the 450,000 acfm Unit #6 absorber. Centrifuge operation and wet cake material handling, although working well in the late stages of the program, were not demonstrated long enough to develop a high level of confidence that all major problems with this equipment have been resolved.

We would reiterate that our confidence level in building a second generation system is high.

Future Plans

The Company has been evaluating the potential expansion of scrubbing at Mystic Station for some time. There are factors in this evaluation beyond the strictly technical which must be seriously considered.

The economic attraction for scrubbing is favorable based on the present price differentials between low and high sulfur fuel oils. The fuel oil energy picture is so fluid as to make it extremely difficult to assess the future price differentials. These differentials can be adjusted for reasons other than solely cost and are therefore not readily predicted.

In this period of dire shortage of capital, the Company is looking very hard at all capital committments. Our ability at this time to raise the capital for this project in competition with other company capital requirements is subject to question and concern. Possibilities of funding this project by leasing and/or by revenue bond financing are being explored.

Allowing utilities to burn higher sulfur fuels than is now permitted in Massachusetts is under study. Higher sulfur fuel use will reduce the economic incentive to install scrubbers.

A selective burning program using fuel switching based on meteorological conditions if allowed, would be considerably less costly than stack gas SO_2 control. The rising consumer and energy crisis pressures may redirect SO_2 control to this approach.

The President has recently issued a policy statement that the burning of fuel oil in utility boilers be greatly reduced. The impact of this policy on the Mystic Station fuel situation both from a fuel use and a fuel pricing point of view is uncertain.

We do not rule out but we cannot yet commit to scrubber installations at Mystic Station until many of these uncertainties are resolved.

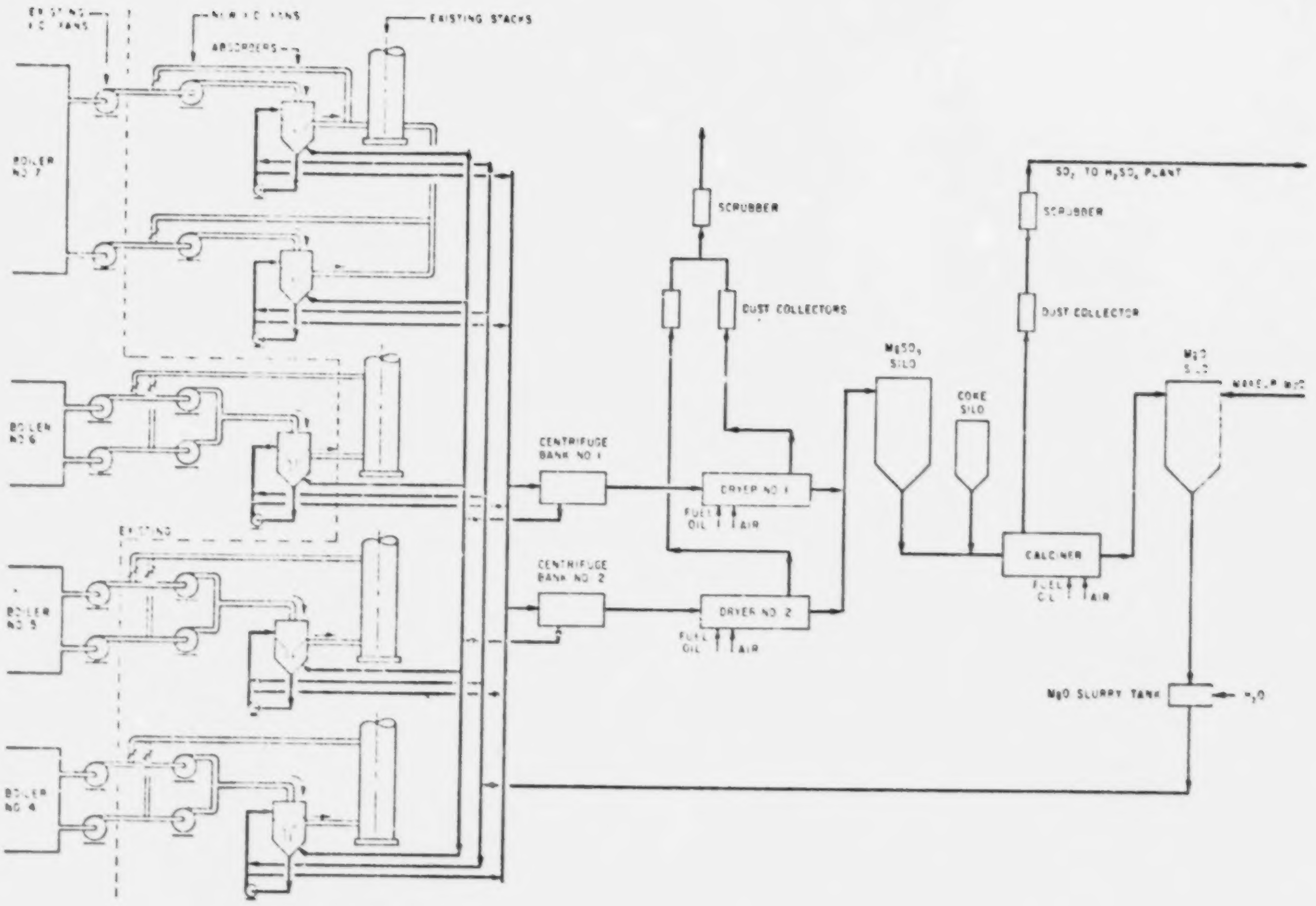
EXISTING I.D. FANS
NEW I.D. FANS
ABSORBERS
EXISTING STACKS
BOILER NO 7
BOILER NO 6
BOILER NO 5
BOILER NO 4
EXISTING
CENTRIFUGE BANK NO 1
CENTRIFUGE BANK NO 2
DRYER NO 1
DRYER NO 2
FUEL OIL
AIR
SCRUBBER
DUST COLLECTORS
MgSO$_3$ SILO
COKE SILO
CALCINER
DUST COLLECTOR
SO$_2$ TO H$_2$SO$_4$ PLANT
MgO SILO
MAKEUP MgO
MgO SLURRY TANK
H$_2$O

FIGURE 1

Expansion Study - Magnesia Scrubbing
Unit Nos. 4, 5, 6, 7
Mystic Generating Station
Boston Edison Company

MAG-OX SCRUBBING

EXPERIENCE AT THE COAL-FIRED DICKERSON STATION

POTOMAC ELECTRIC POWER COMPANY

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ABSTRACT

The paper presents a description of the Chemico-Basic Mag-Ox scrubbing system installed at the Dickerson Generating Station. Operating experiences for the first year of operation are reviewed. Projected costs for future installations are discussed.

MAG-OX SCRUBBING

EXPERIENCE AT THE COAL-FIRED DICKERSON STATION

SYSTEM DESCRIPTION

The Potomac Electric Power Company - PEPCO - in late 1970 in continuation of their search for a stack gas desulfurization system, selected a Chemico-Basic magnesium oxide process for installation at the Dickerson Generating Station. The selected system consists of a two-stage scrubber system sized to process half the flue gas, 295,000 acfm, from the 190 Mw Unit #3. The system is designed as a parallel system with its own wet I.D. fan. With the parallel arrangement loss of the scrubber does not cause any loss of load. The scrubber is capable of taking flue gas from either ahead of or after the existing electrostatic precipitator.

Flue gas enters the first stage, the particulate removal scrubber, where the gas is cooled and saturated from 250°F to 120°F. The flue gas passes through an adjustable throat venturi where the fly ash is removed. The ash-laden water is recycled through the scrubber with a bleed stream carrying ash to the thickeners. The thickener underflow is discharged to a dilution tank where water is added to pump the ash to a settling pond. The overflow from this pond cascades through four ponds. Water from the lowest pond is pumped back to the dilution tank. The thickener overflow is pumped back into the first stage scrubber.

The flue gas leaves the first stage passing through mist eliminators then to the fixed throat venturi where it contacts the recycling MgO slurry for absorption of the SO_2. As the MgO absorbs SO_2 magnesium sulfite crystals build up in the slurry. A bleed stream is sent to the centrifuge where the sulfite crystals are stripped and sent to a rotary oil-fired dryer. The dried $MgSO_3$ is sent to a silo for storage and ultimate shipping to the calciner. The dryer off gas is returned to the inlet of the second stage scrubber.

The mother liquor from the centrifuge is returned to the scrubber. A bleed from the mother liquor is used to slake the MgO. The MgO is fed on demand to the scrubber to maintain a neutral pH.

The flue gas leaves the second stage through mist eliminators to the wet I.D. fan through the mist eliminator tank to the stack where it is mixed with the unscrubbed flue gas from Unit #3 giving a mixed gas temperature of about 175°F.

OPERATIONS

The SO_2 removal system was placed in operation on September 13, 1973. Operation since that time can be divided into four phases as follows:

Phase I	September 13, 1973 to January 14, 1974 - Initial operation and debugging.
Phase II	January 14 to April 15, 1974 - Maintenance and modification.
Phase III	April 1 to July 1, 1974 - Modification verification.
Phase IV	July 1 to December 31, 1974 - Performance testing, optimization and reliability.

The salient features of each phase will be reviewed. Attached to this report is a summary of operations (Appendix A) listing each run, the duration and the reason for shutdown.

Phase I

Initial start-up and operation was reasonably smooth. There were two shutdowns caused by failures of stainless steel expansion bellows allowing first stage slurry to leak into the second stage. Examination verified that the bellows were not made of the specified 316 stainless. The major problem was with the MgO feed system. Continual plugging occurred in the MgO mix tank and suction lines to the MgO make-up pumps.

The longest continuous run during this phase was for 271 hours. Approximately midway through this run the boiler was forced out for 24 hours with a tube leak. All liquid flows and levels were maintained and flue gas returned to the scrubber as soon as the boiler returned to service. This phase concluded when the boiler shut down January 14 for annual maintenance.

Phase II

Inspection of the scrubber system was made after about 700 hours operation. The system was basically in good condition with absolutely no sign of scaling or build-up. However, in the first stage where the operating pH is less than two, there was corrosion of nuts, bolts, hanger rods, spray nozzles, bellows and the vessel itself. Examination determined that all the corroded parts were of non-specified material. There was some very minor corrosion on 316 stainless. The corrosion of the vessel occurred where the protective flake glass lining was penetrated. The problem here was in some part due to improper application and in part due to construction damage after the lining was installed. This represented a very small percentage of the total flake glass lining.

The major modification was the addition of a pre-mix tank in the MgO feed system. Steam sparging was added to the MgO mix tank for future use with recycle MgO. Other minor modifications were made in piping.

Phase III

Operation resumed with start-up on April 15, 1974. The intent was to operate to verify the modifications and then shut down to set up and operate for performance testing. The pre-mix tank improved slaking but not to an acceptable standard for long-term operation. We decided the end of April that the system could be operated for performance testing. We shut down, checked our inventory of MgO and storage space in the magnesium sulfite silo and found we did not have enough MgO to run the test nor storage space for sulfite. At this time we had 130 tons of sulfite at Rumford waiting to be calcined. Boston Edison was using the calciner and it appeared there was no chance of PEPCO's material being calcined before July. Additional virgin MgO had not been ordered as we were expecting to be able to test on recycle MgO. We did operate in May to empty the MgO silo.

Chemico decided to replace the pre-mix tank with a "solids liquid mixing eductor" to improve slaking.

Phase IV

PEPCO received permission to use the EPA owned calciner at Rumford, Rhode Island July 1, 1974. Virgin MgO was on order and we were expecting recycle MgO. Virgin MgO arrived first near the end of July. The first start-up was August 1. The mixing eductor proved totally unsatisfactory - plugging continually. After 10 hours we shut down and re-installed the pre-mix tank which had been modified. Preliminary tests operating on virgin MgO indicated an SO_2 removal in the 70% range. Chemico felt the pressure drop across the absorber throat would have to be increased to obtain the 90% design removal. These modifications were made and the indicated removal efficiency on virgin MgO is in excess of 90%.

Our first recycle MgO was received and introduced into the system on August 16. The dryer feed material became sticky and caused caking in the dryer. This was believed to be caused by unreacted MgO in the centrifuge cake. During the next run steam sparging was used to raise the temperature in the MgO mix tank to correct this problem. It has also been necessary to change the dryer operating temperature on recycle MgO. Slaking with the modified pre-mix tank has been satisfactory on both virgin and recycle MgO.

In conjunction with Chemico, Basic, Essex and EPA, we are currently into a 6-month program to test, optimize operating conditions and gain reliability experience. The system looks encouraging - there has been no problem to rule out the technical feasibility of the Mag-Ox process for SO_2 removal. There are still some problems in the sulfite handling equipment. The equipment is apparently sized for steady state operation. The centrifuge hopper and the dryer tend to hold up material and then release it in a slug that overloads the sulfite conveyors.

A performance test program has been completed by York Research and while formal results are not available, the indicated SO_2 removal efficiency is in the 88% to 96% range as gas flow varies from 150,000 to 300,000 acfm. Particulate removal is in excess of 99% when taking flue gas from either before or after the precipitators.

Operating Summary

We still continue to be plagued with minor problems causing shutdowns. Examples of these are - corrosion leaks in rubber lined pipe, erosion leaks in second stage piping, pump seal problems, bearing failure in sulfite bucket elevator, etc. Operating availability continues to improve - for the month of August it was 43.5% and since August 13 the availability is running 55 to 60%. In contrast to these figures, the availability of the Dickerson units has been around 90% since their installation. A scrubber system should be capable of matching boiler availability. We would therefore recommend the installation of a scrubber by-pass system rather than spare scrubber capacity until more experience is obtained on long-term reliability.

Economics

When PEPCO started investigating scrubbers in 1969 the estimated capital cost of a scrubber system was $12 to $20 per kilowatt. In the

January 1974 EPA report on the October 1973 scrubber hearings the capital cost was given as $50 to $65 per kilowatt. PEPCO's current in-house estimate in 1974 dollars is in excess of $100 per kilowatt.

Operating costs are difficult to estimate as we do not have sufficient information on MgO make-up required or a real estimate of the maintenance costs. Based on our present experience, it will require two additional operators per shift.

The estimated increase in power cost for the Dickerson Station operating at an 85% capacity factor would be about 5 mills per kilowatt hour of which over 3 mills is the fixed charge on investment. These costs assume a recovery system through on-site production of SO_2 gas. The assumption is made that the sale of elemental sulfur or sulfuric acid will cover all fixed and operating costs associated with an on-site sulfur or acid plant. We realize that this is a debatable assumption, but at this time we do not have a good estimate for this cost. For instance, a chemical company operating an acid plant would have to be guaranteed a continuous feed for the plant. What will be the availability of a scrubber system? What will be the variation in sulfur content of coal? These are the kind of questions that will have to be resolved to arrive at definite costs.

CONCLUSION

PEPCO entered into the development of stack gas desulfurization based on an analysis of low sulfur fuel availability and the projected costs of these systems. Throw-a-way systems were rejected as at our particular plant sites, the sludge disposal would cause more environmental problems than the removal of sulfur dioxide would solve. We believe these were correct decisions based on the then available data.

Where do we stand after six years and expenditures approaching $9,000,000? The Mag-Ox process shows promise as a means of removing sulfur dioxide from flue gas. The SO_2 can be absorbed, the sulfite crystals can be removed and a marketable sulfuric acid can be produced. There are still some problems to be solved. These problems are:

1. MgO - is there a limit to the number of times it can be recycled? To date, we have been through only one cycle.

2. Material balance - it must be determined how much make-up MgO is required and whether any MgO is being lost in an environmentally unacceptable manner.

3. Long term reliability and availability must be demonstrated. This is a material selection problem to select the best material to stand up under corrosion and erosion attack.

4. Economics.

The economic situation has changed so drastically that decisions on future installations must be based on a valid cost-benefit analysis for each specific location. For example, we are required by the State of Maryland to maintain at each plant a seven day supply of fuel containing less than 1% sulfur. This fuel is to be used on order from the State when there is an air pollution problem in the area. This fuel has been on-site for almost three years and we have never been ordered to use it. This indicates to me that sulfur dioxide has not been a health problem in any of the pollution alerts.

PEPCO continues to analyze the status of various stack gas desulfurization systems, the availability of low sulfur fuels, coal gasification, solvent refined coal and any other method for meeting our obligation to produce reliable power with a minimal adverse impact on the environment.

APPENDIX A

SUMMARY OF OPERATIONS
CHEMICO-BASIC MgO SULFUR REMOVAL SYSTEM
DICKERSON UNIT 3
POTOMAC ELECTRIC POWER COMPANY

1. Run #1 - September 13, 1973 for 36 hours
   Shutdown - failed stainless bellows in first stage flow to recycle pump suction.

2. Run #2 - September 24 for 10 hours
   Shutdown - MgO feed problems - could not control pH

3. Run #3 - October 1 for 60 hours
   Shutdown - plugged MgO tank and lines

4. Run #4 - October 12 for 30 hours
   Shutdown - failed stainless bellows in first stage flow to recycle pump suction (Not same bellows as #1)

5. Run #5 - November 6 for 13 hours
   Shutdown - bearing failure $MgSO_3$ bucket elevator

6. Run #6 - November 8 for 51 hours
   Shutdown - boiler outage - blown tube

7. Run #7 - November 12 for 54 hours
   Shutdown - erosion corrosion leak - first stage slurry line to thickeners

8. Run #8 - November 30 for 24 hours
   Shutdown - lost fuel oil to dryer

9. Run #9 - December 1 for 2 hours
   Shutdown - lost fuel oil to dryer - underground fuel oil line failure

10. Run #10 - December 9 for 138 hours
    Shutdown - boiler outage - tube leak (maintained all scrubber flows and levels during 24-hour boiler outage)

11. Run #11 - December 16 for 109 hours
    Shutdown - partial pluggage of MgO feed lines was restricting gas flow to scrubber

12. Run #12 - January 6, 1974 for 192 hours
Shutdown - boiler off for scheduled overhaul and partial plugging of MgO

Summary

September 13, 1973 to January 14, 1974 - 719 hours operation and scrubber available for 70 hours that boiler was unavailable.

Scrubber Availability = $\frac{789}{2952}$ = 26.7%

December 9, 1973 to January 14, 1974

Scrubber Availability = $\frac{463}{864}$ = 53.6%

13. Run #13 - April 15, 1974 for 17 hours
Shutdown - flop gate in $MgSO_3$ screw conveyor

14. Run #14 - April 16, 1974 for 13-1/2 hours
Shutdown - Solidified MgO in pre-mix tank, K-Tron MgO weigh feeder

15. Run #15 - April 22, 1974 for 10 hours
Shutdown - centrifuge hopper filled - bucket elevator tripped - leak in 1st stage pinch type control valve

16. Run #16 - April 25, 1974 for 89-1/2 hours
Shutdown - bucket elevator tripped - mother liquor line to pre-mix tank plugged

17. Run #17 - April 29, 1974 for 43 hours
Shutdown - not forced - to make minor modifications - restart will be for test program

Availability April 15 to May 1 = $\frac{173}{389}$ = 40.5%

18. Run #18 - 9:40 am, May 13 to about noon on May 17 - 100 hours
Shutdown - Out of MgO @ 6:45 am on May 17 - continued to operate to empty MgO tank and strip crystals - bucket elevator shaft broke

19. Run #19 - August 1 for 10 hours
Shutdown - Test solids-liquid mixing. Eductor-plugged-down to replace with pre-mix tank.

20. Run #20 - August 6 for 54 hours
Shutdown to install throat restrictor

21. Run #21 - August 13 for 24 hours
Shutdown - offloading overweight $MgSO_3$ truck plugged conveyor dryer to silo

22. Run #22 - August 15 for 64 hours
Shutdown recycle M_2O caused caking in dryer

23. Run #23 - August 20 for 12 hours
Shutdown - bucket elevator would not handle flow of $MgSO_3$

24. Run #24 - August 26 for 84 hours
Shutdown - leak in 14" elbow

August summary operation 248 hours 33.2%
Available 323 hours 43.5%

25. Run #25 - September 3 for 28 hours
Shutdown - leak in 14" elbow

26. Run #26 - September 6 for 28 hours
Shutdown - 8" flex valve failed

POWER PLANT FLUE GAS DESULFURIZATION
by the
WELLMAN-LORD SO_2 PROCESS

PART I

THE DEAN H. MITCHELL STATION
(Northern Indiana Public Service Company)

by

E. L. Mann
Plant Engineering
Northern Indiana Public Service Company
Michigan City, Indiana

PART II

CONTINUING PROGRESS FOR THE WELLMAN-LORD SO_2 PROCESS

by

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Lakeland, Florida

Prepared for Presentation at

Flue Gas Desulfurization Symposium
Sponsored by the Environmental Protection Agency
Atlanta, Georgia
November 4-7, 1974

THE

DEAN H. MITCHELL STATION
(NORTHERN INDIANA PUBLIC SERVICE COMPANY)

WELLMAN-LORD (DAVY POWERGAS INC.)
ALLIED CHEMICAL CORPORATION

SO_2 EMISSION CONTROL FACILITY

BY

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Michigan City, Indiana

ABSTRACT

In a jointly funded EPA-NIPSCo. project, the Northern Indiana Public Service Company will combine two technologies to provide a flue-gas-desulfurization system in a 115MW pulverized coal-fired boiler at the Dean H. Mitchell Station in Gary, Indiana. The SO_2 controls will be back-fitted onto a unit which went in service in 1970. These systems, scheduled to go into service in late 1975, are The Wellman-Lord SO_2 Recovery Process which will produce a concentrated SO_2 gas and the Allied Chemical SO_2 Reduction Process which will produce high quality elemental sulfur having a minimum assay of 99.5%. This quality is suitable for sulfuric acid production.

Following acceptance tests at the conclusion of construction, a one-year period of operation by Allied Chemical will be funded entirely by NIPSCo.. A comprehensive emission-testing program will be conducted by EPA during this period. In this final phase, severe test conditions and refinements will be imposed on the system consistent with safe operation of Unit 11 and evaluated by NIPSCo. and the EPA, each evaluating in his respective area of concern. The EPA and NIPSCo. expect to use the data obtained to extrapolate to obtain costs and other data for larger facilities.

Prepared for Presentation at
Flue Gas Desulfurization Symposium
Sponsored by the Environmental Protection Agency
Atlanta, Georgia
November 4-7, 1974

THE

DEAN H. MITCHELL STATION
(NORTHERN INDIANA PUBLIC SERVICE COMPANY)

WELLMAN-LORD (DAVY POWERGAS INC.)
ALLIED CHEMICAL CORPORATION

SO_2 EMISSION CONTROL FACILITY

Northern Indiana Public Service Company is a combination gas and electric utility operating in the Northern third of the State of Indiana. The Company has 3 coal fired stations in operation, each station being between 600 and 700MW in capacity. Each is located in environmentally sensitive areas. The stations have used Mid West coal of 3 to 4% sulfur, 10% ash and 11,000 plus BTU/lb..

In seeking a suitable method for cleaning flue gases of SO_2, NIPSCo. concentrated on finding a system that would be totally acceptable on all environmental fronts. Water and land use in the area indicated that a "throw-away product" removal system would not be acceptable. It also appeared that recovery of the sulfur in the form of SO_2, sulfuric acid, or any other sulfur compound might prove to be a problem at some future date when it came to marketing or disposing of the product.

Combining two proven processes appeared the best assurance of meeting all environmental requirements. The Wellman-Lord SO_2 Recovery Process is meeting, or exceeding, required emission standards in treating tail gases from several sulfuric acid and sulfur recovery plants in the U.S. and Japan and at a Japanese 70MW oil fired generating plant and a 220MW oil fired peaking unit in Japan. Allied Chemical's process has been demonstrated in Canada, where it operated a system recovering elemental sulfur from the Falconbridge nickel mine's 13% SO_2 smelter gas.

Furthermore, the information which we had indicated that retrofitting some units with a throw-away system could be about the same capital cost as a recovery system.

Initial discussions involving Davy Powergas, Allied Chemical Company, Northern Indiana Public Service Company and the EPA took place early in 1972. The EPA and NIPSCo. reached agreement on a contract in June, 1972.

The EPA-NIPSCo. contract and, in turn, the NIPSCo.-Davy Powergas contract has requirements for an emission control system which will operate at a minimum of 90% SO_2 removal from the flue gases of the 115MW boiler while feeding coal with a sulfur content of 3.5%. The process also is guaranteed not to allow any emission in excess of 200 ppm by volume of SO_2 in the exit gas with lower sulfur fuel. An existing electrostatic precipitator is expected to reduce the dust loading to 0.044 grains per actual cubic foot at the scrubber inlet. The Davy Powergas system is being designed with a pre-scrubber to remove 0.2 grains per ACF with the capability of handling considerably greater fly ash loadings for short periods. Ash content of the Midwest Coal is 10.6%, the BTU content 11,008/lb..

The ductwork between the existing I.D. Fans and the 236 foot tall chimney will be revised so as to divert the flue gases, 320,000 acfm at 300°F, to the new installation. A booster fan will be installed between the I.D. Fans and the SO_2 system. The flue gases, after treatment in the scrubber system, will be reheated to 180°F by a direct fired gas reheater. The release of the treated flue gases will be at a point about 165 feet above ground level through a stack on the top of the absorber. A by-pass back to the original stack is being installed. The flue gases enter the SO_2 absorber relatively free of particulate matter. The Wellman-Lord system employs a sodium-sulfite rich solution of sulfite and bisulfite to remove the SO_2 from the stack gas. The resulting bisulfite rich solution is pumped to a regeneration unit in which the reaction is reversed in an evaporator/crystallizer. The application of heat from a 50 psig steam system generates water saturated SO_2 and sodium sulfite crystals which are separated, redissolved and recycled as clean absorber feed. Caustic soda or soda ash is added to replenish the system.

Some sodium sulphate is formed in the Wellman-Lord system. A small purge stream is continuously withdrawn to prevent a sulfate buildup in the system. Sulfates and a small amount of sulfites in the purge amount to approximately 8 to 10% of the sulfur coming into the system.

The output of the Wellman-Lord plant is a gas stream of about 85% SO_2, the remainder mostly water vapor. The SO_2 feed stream is received by the Allied reduction plant. The gas is compressed by a blower and mixed with natural gas which serves as a reductant.

The stream then enters the primary reaction system consisting of two packed-bed regenerative heat exchangers and a catalyst-packed reduction reactor. The two heat exchangers operate cyclically, one giving up heat to the entering gas mixture while the other is being reheated by exit gas from the exothermic reaction. Periodic reversal of the gas flow through the heat exchangers provides essentially stable operating conditions in the reactor.

After exiting from the regenerative heat exchanger, gas from the primary reactor passes first through a sulfur condenser, which removes the elemental sulfur for storage in molten form. The remaining gas mixture then enters a two-stage Claus unit containing an interstage condenser, which also removes elemental sulfur to storage. A final sulfur condenser removes the last portion of the elemental product, and the unrecovered sulfur values in the tail gas are oxidized to SO_2 and finally returned to the absorber of the Wellman-Lord SO_2 Recovery Process.

The contracts between NIPSCo. and EPA and the other principals, Davy

Powergas and Allied Chemical, contain penalty-assessable guarantees for the following: SO_2 emission levels - The process, according to the contracts, will be at least 90% efficient firing coal with a sulfur content of up to 3.5% (approximately 2,300 ppm by volume of SO_2 in the stack gas). As an override, no more than 200 ppm by volume of SO_2 will be present in the exit gas.

Mechanical reliability - The process plants will be mechanically sound.

Utilities consumption - The aggregate cost of steam, electric power, and natural gas required for operation of the complex will not exceed a specified cost; i.e., $56.00 per hour based on:

Electric Power - $0.007 per KWH
Steam - $0.50 per 1000 lb. at 550 psig, 750°F
Natural Gas - $0.55 per million BTU.

Chemicals requirements - The quantity of make-up chemicals (caustic soda or soda ash) will not exceed a fixed daily amount. The average chemical make-up over a twelve (12) day operating period at an average of 92MW shall be no greater than 6.6 tons per day of NA_2CO_3. The value of antioxidant used during the 12-day period shall not exceed an average of $400 per day at an average of 80% load factor.

Product quality - Sulfur produced is to have a quality suitable for use in the manufacture of sulfuric acid by the contact process.

It is recognized that the demonstration system is not intended or designed to reduce emissions other than SO_2 and particulates. Reduction of other pollutants by the demonstration system is incidental to the demonstration objectives. Therefore, the required compliance with current emission regulations shall apply only to particulates and SO_2.

If the project were completely financed by NIPSCo., we calculate the following data.

Capitalization, including top charges, escalated to 1975- $13,441,434

This is $117/KW installed capacity or $12,000 per million BTU/Hr.input.

Operation & Maintenance, including cost of capital * - $4,977,186 (based on 72% load factor)

This is 6.3 mils/KWH gross generated or 65 cents per million BTU coal burned.

We, at NIPSCo., are looking forward to the results of this demonstration project. We hope the data we and the EPA obtain will be of value in the decision making of others.

* Includes management fee, Allied process license (Davy Powergas Inc. process license does not apply to this project).

Based on 10 year plant life.

CONTINUING PROGRESS
FOR
WELLMAN-LORD SO_2 PROCESS

by

E. E. Bailey
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Flue gas desulfurization for two large utility boilers, will be the second application of the Wellman-Lord SO_2 process on a coal-fired power plant. In Japan there are presently four successfully operating Wellman-Lord SO_2 plants on oil fired, power and steam generating plants.

Capital and operating costs for the Wellman-Lord flue gas desulfurization plant can be minimized by the proper selection of design criteria.

This paper will present a brief outline of the above new project. Coverage will also be given to some of the Wellman-Lord installations in Japan. Finally a section on critical design criteria will be presented to emphasize savings in capital and operating costs.

The client has contracted to build two coal-fired power plants and although the coal that would be burned in both of these power plants was low in sulfur content -- .8% to 1.3% -- it was still necessary for each plant to be suitably equipped with a sulfur dioxide and particulate removal facility. Burning the low sulfur coal and installing electrostatic precipitators for fly ash collection would bring these power plants - 330 MW and 340 MW - very close to meeting the Federal Emission Standards. State standards, however, require that pollution control facilities be installed.

TABLE 1 - Comparison of NonControlled Emissions With Existing Federal and State Air Pollution Regulations

	Sulfur Dioxide Stack Concentration		Particulate Stack Concentration	
	ppm	lbs/MM BTU	Grains/acf	lbs/MM BTU
UNIT NO. 1				
Avg. Grade Coal	700	1.98	0.026	0.104
Low Grade Coal	1150	3.25	0.044	0.175
UNIT NO. 2				
Avg. Grade Coal	700	1.96	0.039	0.154
Low Grade Coal	1150	3.23	0.062	0.245
FEDERAL STANDARDS (As of June 1974)		1.2		0.10
STATE STANDARDS (As of Sept. 1973)		.34		0.05(Max) 0.02(2)

The task of selecting a suitable sulfur dioxide-particulate removal process was performed by the client and their engineer/architect for the two power plants. Preliminary inquiries were solicited and studies were made of existing power plant pollution control technology. Following completion of these studies, a detailed bid specification was prepared. After evaluation of all bids by the Client, the sulfur dioxide-particulate removal project was awarded to Davy Powergas for installation of its Wellman-Lord sodium sulfite/bisulfite process in combination with the Allied Chemical Corporation SO_2 reduction process for the production of elemental sulfur.

DESCRIPTION OF PROCESS

The entire sulfur dioxide-particulate removal facility will consist of a gas handling area for each power plant, an absorbing solution regeneration plant, an area for the reduction and concentration of a by-product purge stream and finally an elemental sulfur plant using Allied Chemical Corporation's technology.

Each gas handling area is designed to process 1,588,000 acfm of gas containing between 700 ppmv - 1200 ppmv sulfur dioxide. The fly ash loading of the incoming gas will range between 0.06 and 0.04 grains/acf. The flue gas from each power plant is picked up at the stack entrance by three hot side fans, operating in parallel. THe discharge pressure from each fan is sufficient to force the flue gas through a wet venturi type prescrubber and a tray type sulfur dioxide absorption tower. Each booster fan is directly connected to its own venturi and absorber. The cleaned gases from each of the absorbers are combined for reheat before re-entering the power plant stack for discharge to the atmosphere. Each power plant flue gas handling area has one spare fan, venturi and absorption tower at the request of the Client.

The sulfur dioxide rich absorbing solution from both power plant gas handling trains is collected at a central point before being processed in the regeneration area. This central collection point provides storage of rich absorber solution. It also provides a supply of lean absorber solution so that the regeneration area may be shut down for seven (7) to twenty-four (24) hours for maintenance and operational clean out requirements without affecting the plant's SO_2 removal capability.

The chemical regeneration area consists of two parallel, double effect, forced circulation evaporators. The rich absorbing solution is thermally regenerated by driving off sulfur dioxide and water vapor. This vapor passes through a series of partial condensers where the sulfur dioxide vapor is concentrated to 85 vol. %, compressed and forwarded to the Allied sulfur plant. The regenerated absorbing solution leaving the evaporators is combined with stripped condensate from the partial condensers and recycled back to the absorbing solution storage area.

A slip stream of absorbing solution is taken from the absorbers on both power plants for processing in a purge treatment area. Through a series of unit operations the inactive sodium salts are concentrated and removed from the remaining absorbing solution. The final purge liquor will then be dried and the resulting product - 85 wt % Na_2SO_4 - will be marketed. As a result of this purge treatment area, the chemical make up requirement can be reduced by a factor of 4. Therefore the chemical make-up cost for a plant of this size would be reduced by some $2.7 million per year with the installation of a purge treatment area.

The Allied sulfur plant consists of two identical, parallel trains, each capable of producing 60 LTPD of sulfur.

The sulfur dioxide-water vapor which enters the sulfur plant is reacted with natural gas over a catalyst, generating a mixture of hydrogen sulfide and sulfur dioxide. This resulting gas then passes through a series of Claus reactors, generating sulfur and an off gas which is incinerated and recycled to the gas handling areas. The sulfur produced will have a purity of 99.9% and will be marketed.

PROJECT SCHEDULE

The compliance date for this power plant is July 1, 1977. By this date both of the gas handling, sulfur dioxide-particulate removal facilities must be operating successfully to meet both the State and Federal air pollution abatement regulations. Since the project was awarded in the Spring of 1974 and expected start up is early 1977, the total length of this project through engineering, design, procurement and construction is planned for thirty (30) to thirty-three (33) months.

PURGE REDUCTION PROGRAM

The Wellman-Lord process is, like all other alkali scrubbing processes, plagued by oxidation and disproportionation of the sodium sulfite/bisulfite absorbing solution. Whatever the mechanism is for breaking down the active sodium salts, it is difficult to reverse this action to rejuvenate the inactive sodium. Therefore, all inactive sodium salts presently must be purged from the system and their sodium ions replaced by active sodium ions in the form of soda ash or caustic soda.

Due to the waste purge streams, Davy Powergas has been attempting for two years to find or develop a process for reactivating the sodium ion. A number of processes have been investigated, especially those related to the pulp and paper industry where the chemistry is very similar. Preliminary laboratory scale tests and even one full scale plant test have been run on the different available processes. Since this development program is of a highly confidential nature, the specific processes and the results of the tests conducted will not be discussed.

However, a few processes do look promising. Engineering for a demonstration unit will probably begin early in 1975. Additional tests are being conducted this Fall to determine the most applicable process ard the necessary scale up factors which will be required for the demonstration unit. Location of the planned demonstration unit has not been chosen, but it will probably be in the United States at one of the existing, or possibly new, Wellman-Lord sulfur dioxide recovery plants.

In searching for this purge reduction process, Davy Powergas is not looking for a mechanism to reactivate the sodium ion at the expense of a "More Easily Disposed of Product" or by-product that "can be sold" but that nobody wants to buy, but instead we hope to close the loop by generating sodium carbonate. In closing the loop we intend to reactivate as much of the inactive sodium ion as economically feasible. But, even if this is 100% successful, there still must be some waste purge stream due to the build up of make up material contaminants. Details of the specific demonstration plant will be the subject of a later paper.

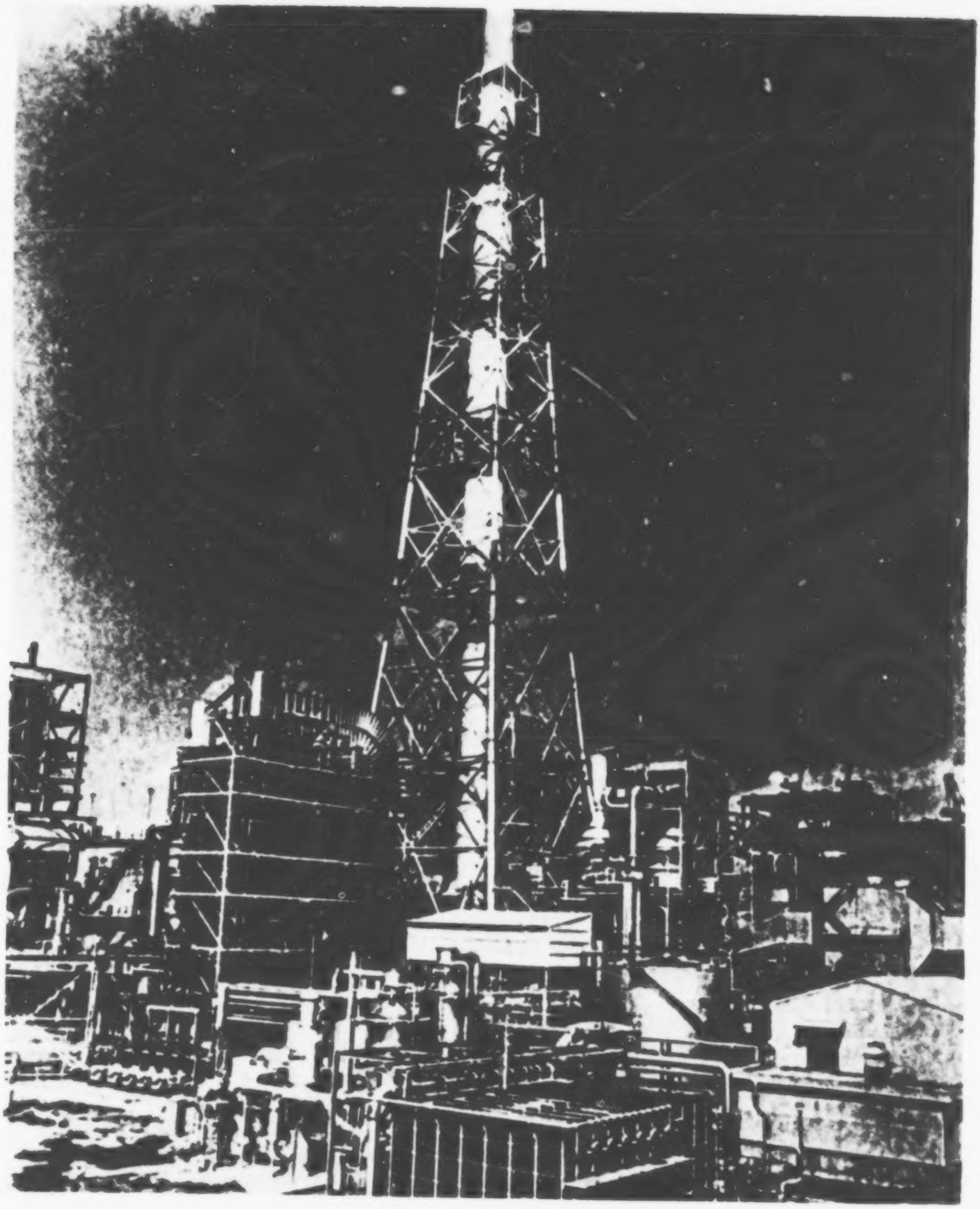
FLUE GAS DESULFURIZATION IN JAPAN

The Wellman-Lord process has been installed on an oil-fired, 220 MW power plant for Chubu Electric Power Company in Nagoya, Japan. This installation was designed and constructed by one of our Japanese licensees, Mitsubishi Kakoki Kaisha, and came on stream in late Spring of 1973. This particular power plant is a peaking station; therefore, the gas handling-SO_2 absorption equipment must be capable of handling load variations of from 35% to 105% of design flow a number of times each day. Also to be considered is the suspension of power plant operation for the weekend.

This weekend suspension is handled by the installation of ample absorbing liquor surge capacity so that the chemical plant area and the sulfuric acid plant (end product) can operate at low rates. When the power plant is brought back on line after the weekend suspension of operation, the flue gas sulfur dioxide absorption area is started up automatically. This automatic start up and any subsequent suspension of operation of the entire desulfurization plant can be handled from the control room. As a result of this highly automated system the entire operation of the desulfurization plant, including start up and shut down, can be handled by two operators.

Although the Wellman-Lord sulfur dioxide recovery system installed at Japanese Synthetic Rubber Company in Chiba, Japan is not on an electric power plant it is still worthy of mention because of its highly successful operating history. This unit is installed on two oil-fired boilers, each generating 185,000 lbs/hr of steam, and it handles about 124,000 scfm of flue gas. The plant started up in June 1971 and maintained a 97% stream time availability in its first year and a 100% stream time availability its second and third years of operation. This sulfur dioxide recovery plant is removing more than 90% of the SO_2 from a flue gas containing approximately 2100 ppmv SO_2.

At the present time there are ten (10) active projects for the installation of Wellman-Lord flue gas desulfurization plants on oil fired boilers in Japan. These ten plants are being designed and constructed by the two Japanese Wellman-Lord licensees. The total boiler exhaust gas to be desulfurized is in excess of 4 million actual cubic feet per minute.



Overall View of Wellman-Lord SO_2 Installation
At Chubu Electric Power Plant, Nagoya, Japan

DESIGN CRITERIA AND HOW THEY AFFECT COSTS

Although many design criteria must be considered when designing any sulfur dioxide-particulate removal facility, there are also several process criteria that should be considered carefully by both the client and by Davy Powergas when designing a Wellman-Lord SO_2 Recovery System. In this section we will highlight the most influential criteria and point out ways to minimize their affect on the plant design. The criteria covered will include: SO_2 content of the gas, water content of the gas, oxygen and sulfur trioxide concentrations of the gas, fly ash loading and expected removal, and total flue gas quantity.

SULFUR DIOXIDE CONCENTRATIONS

Since sulfur dioxide removal is the primary function of this process, SO_2 concentrations in the feed gas have no maximum or minimum limitations. The normal minimum SO_2 concentration in the processed exhaust gas is 200 ppmv; however, lower concentrations can be achieved if necessary.

The size of the SO_2 absorption area is mainly a function of the flue gas flow rate which is governed by the size of the power generating unit; however, the sulfur dioxide concentrations, in and out, do affect the number of mass transfer stages required in the absorber. Generally speaking, a flue gas with a sulfur dioxide concentration of 1200 ppm requiring 90% removal will take four (4) to five (5) stages. Flue gases with higher concentrations - say 3000 ppm, requiring 95% removal - may need only three (3) stages. The difference is due to the higher driving force of the higher SO_2 concentration gas. Each trayed stage will require a minimum of three (3) inches water pressure drop. Using an airfoil booster fan, this may mean as much as $22,120 per year additional operating cost for each additional mass transfer tray installed on a 100 MW power plant.

The chemical plant and any subsequent final product plant, elemental sulfur or sulfuric acid, will be directly affected by SO_2 concentrations in the flue gas. Each 1000 ppmv of SO_2 removed from the exhaust gas of a 100 MW power plant represents approximately 15 LTPD of elemental sulfur or 50 TPD of 100% sulfuric acid. Concentrations of less than 2000 ppmv SO_2 in the flue gas increase the size of the chemical plant on a per pound of SO_2 absorbed basis. This is due to the higher absorbing solution circulation rate and subsequent higher pounds of water vapor per pound of sulfur dioxide evaporator boil up required.

WATER CONTENT OF FLUE GAS

The water content of the flue gas for a given dry bulb temperature will have a direct affect on the number of stages required to satisfy the sulfur dioxide removal requirements. The absorber section of the gas handling train will operate at a temperature 4°F to 12°F higher than the adiabatic saturation temperature of the flue gas. Since this operating temperature of the absorbing section will affect the SO_2 equilibrium, a 2.0 volume % change in water content of the flue gas may require one additional mass transfer unit.

OXYGEN AND SULFUR TRIOXIDE CONTENT OF FLUE GAS

The formation of inactive sodium salts caused by the oxidation of sodium sulfite is directly proportional to the amount of oxygen and sulfur trioxide contained in the flue gas. Therefore, the area most affected by these component concentrations is the Purge Treatment Area. The size of this area is almost directly proportional to the oxygen content of the flue gas. The amount of by-product sodium sulfate formed for each one percent oxygen in the flue gas from a 100 MW power plant is approximately 1.3 TPD.

FLY ASH LOADING AND PERCENT REMOVAL

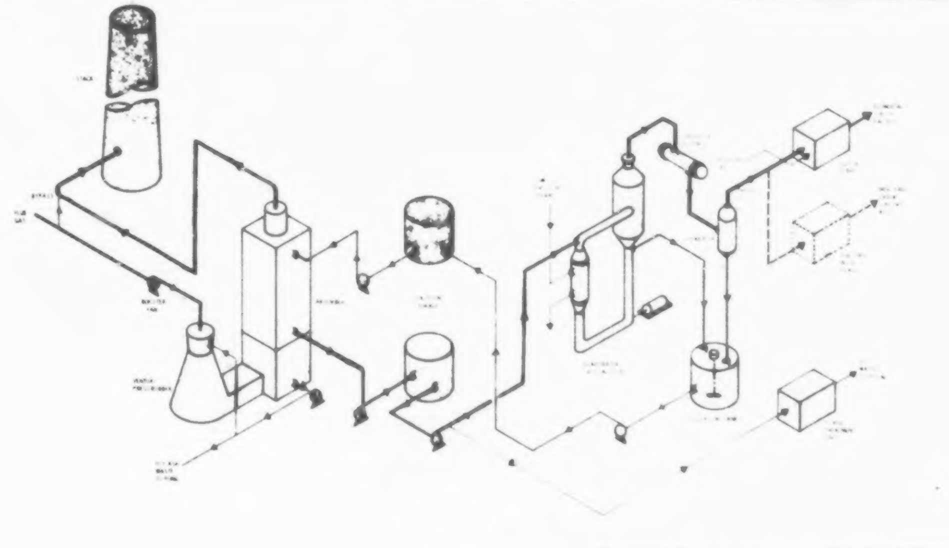
The most economic removal of fly ash from a power plant flue gas is accomplished by combining an electrostatic precipitator with a wet scrubber. Since a wet scrubbing type device (Prescrubber) is used as a gas saturation unit on the Wellman-Lord process, its use to effectively and efficiently remove fly ash particles must be investigated. When sizing the prescrubbing equipment careful attention must be paid to the actual fly ash loading, the percent removal required and the particle size distribution of the fly ash in the gas to the prescrubber.

The more critical the prescrubber design criteria becomes (lower grain loading, higher removal efficiencies, smaller particle size) the higher the energy required to meet the demands. Each additional inch of water pressure drop across the prescrubbing unit will cost approximately $9130 in operating cost per year for a 100 MW power plant when using a radial blade booster fan.

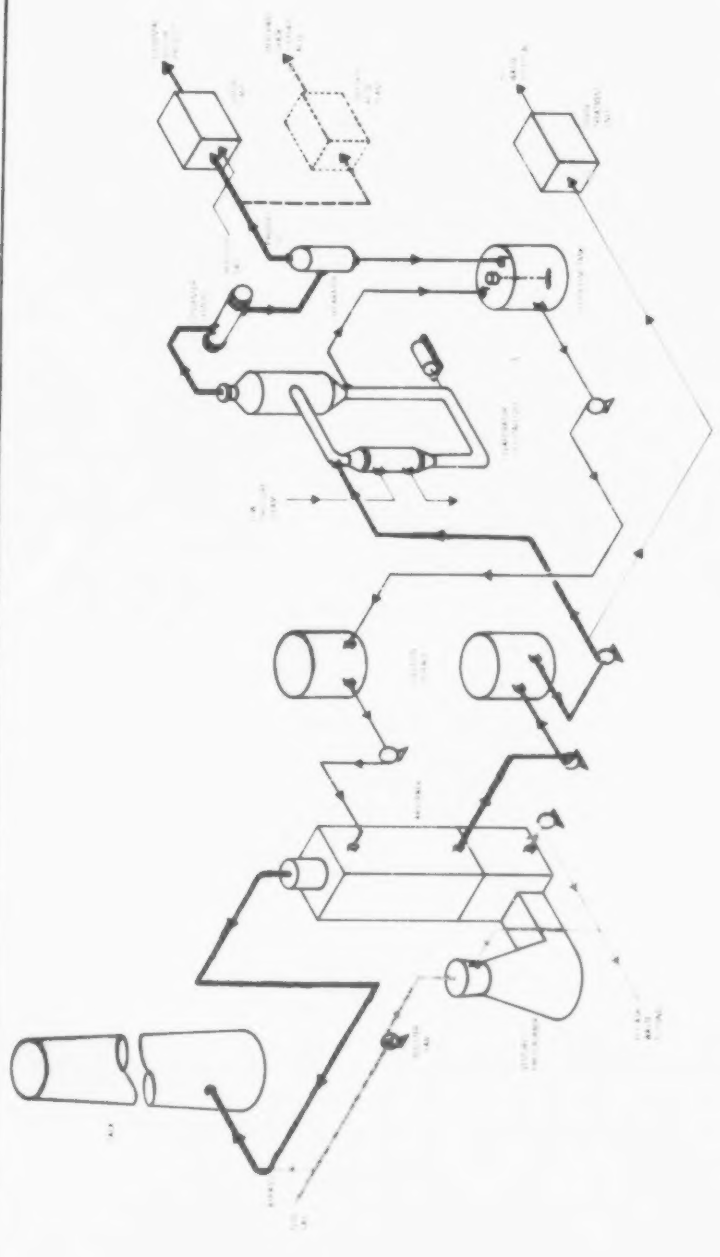
Another design parameter which must be considered is the disposal of the captured fly ash. This captured fly ash is usually in the form of a 1 to 10% by weight slurry in very acidic water. Depending on the overall fly ash removal equipment, this fly ash stream may be blended with the dry electrostatic precipitator fly ash or it may require neutralization and solids concentration before disposal.

FLUE GAS QUANTITY

Although the sulfur dioxide concentration and the fly ash loading of the power plant flue gas play an important role in the sizing of the gas handling area, the quantity of flue gas has by far the largest affect. Since our operating history to date has shown better than 96% on stream time for our absorption areas we do not recommend spare units, but instead suggest that the design be based on a realistic maximum gas flow. To date it has been our recommendation that a modular concept be used in the gas handling area. The present maximum size blower, prescrubber and absorber module would have a gas handling capacity equivalent to a 120 - 150 MW coal-fired power plant.



**WELLMAN-LORD SO_2 RECOVERY PROCESS
(UTILITY INSTALLATIONS)**



WELLMAN-LORD SO_2 RECOVERY PROCESS
(UTILITY INSTALLATIONS)

APPENDIX A

DETAILED PROCESS DESCRIPTION

The Wellman-Lord Sulfur Dioxide Recovery Process is a chemical absorption, thermal regeneration process using an active sodium based absorbing solution. The total processing plant consists of a gas handling area, a chemical regeneration area and a purge treatment area. The description which follows will emphasize the removal and recovery of sulfur dioxide from power plant flue gas.

ABSORPTION AREA

The primary function of the Absorption Area is to remove the sulfur dioxide from the flue gas. Secondary functions of gas saturation, particulate removal and exhaust gas reheat are also accomplished.

The flue gas leaving the power plant air preheaters (or electrostatic precipitators) at 250°F to 300°F and essentially atmospheric pressure is picked up by large booster fans. These fans impart sufficient static pressure to force the gas through the entire gas handling train and out the stack. The gas discharging from the blower will first enter a gas-saturation, prescrubbing unit. The amount of fly ash contained in the gas, the size distribution and the required percent removal will dictate the unit type and size and pressure drop required. The prescrubber will remove fly ash by recirculation of an acidic water-fly ash slurry through a venturi type or a valve tray type unit. Saturation of the flue gas also occurs in the prescrubber, adiabatically reducing the gas temperature to 120-130°F. At the exit of the prescrubber, chevron demisting devices minimize fly ash carry over into the absorbing section. Either all or a portion of the prescrubber is housed in the lower one-third of the absorption tower.

The relatively particulate-free, saturated flue gas now passes into the sulfur dioxide absorption section of the tower. The removal of sulfur dioxide from the flue gas is achieved by a chemical absorption process. A solution which is rich in sodium sulfite enters the top of the column and is converted to a solution rich in sodium bisulfite as sulfur dioxide is absorbed. The mass transfer medium used in the absorption tower will be a series of sieve or valve trays. Due to the extremely low liquid to gas ratio required for absorption, each set of trays requires recirculation of the absorbing solution. This recirculation provides the necessary amount of liquid required to hydraulically load the valve trays.

The absorbing solution rich in sodium bisulfite leaves the bottom of the absorbing section for processing in the chemical plant area. The degree of conversion, amount of sodium sulfite converted to sodium bisulfite, of the absorbing solution is important because it governs the size of the chemical plant and the amount of steam required to regenerate the sodium bisulfite to sodium sulfite.

Clean flue gas passes through either a mesh pad or chevron type demisting section when leaving the absorbing section. This demister minimizes absorbing solution carryover into the power plant stack.

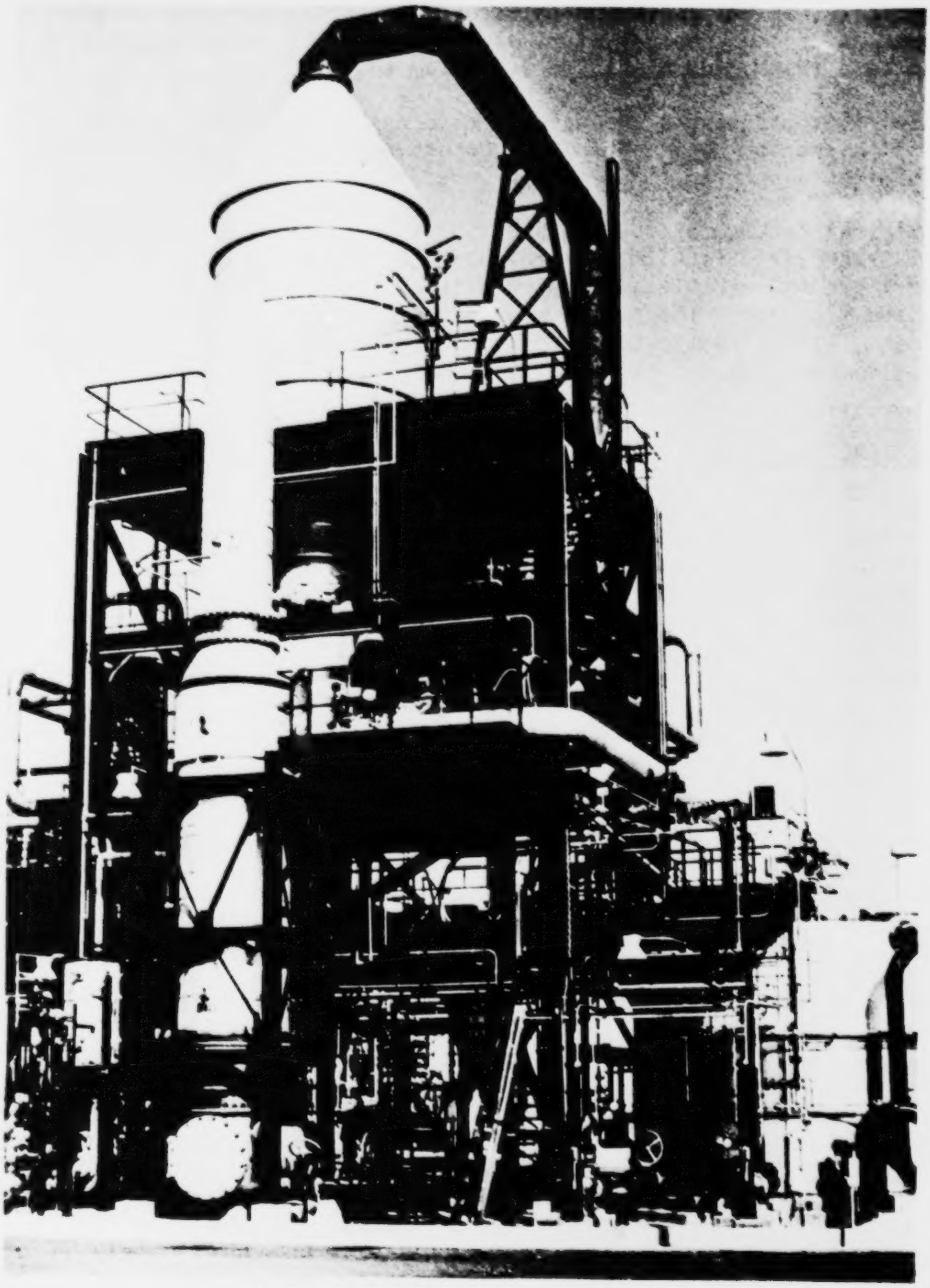
The final section of the gas handling area is a stack gas reheater. This reheater will eliminate the plume, provide bouyancy to the exhaust gas and minimize corrosion of the stack by supplying superheat to the flue gas. The amount of reheat can vary, depending on stack height, area climatic conditions, and materials of construction, but usually requires a 50°F increase in gas temperature.

CHEMICAL PLANT AREA

Thermal regeneration of the bisulfite rich absorbing solution is accomplished in a forced circulation, vacuum evaporator. The sodium bisulfite in the feed solution is thermally converted to sodium sulfite by driving off sulfur dioxide overhead. Water vapor is also removed overhead in an amount which is necessary to satisfy the water balance on the absorbing solution. The sodium salts remaining in the evaporator circulating liquid now form a crystalline slurry. The major component of this crystal is sodium sulfite. The concentration of crystals in this evaporator circulation slurry is kept at an optimum level in order to reduce heat transfer area fouling and decrease evaporator size.

The overhead sulfur dioxide-water vapor mixture is concentrated through a series of partial condensers. Depending upon the size of the chemical plant, which is based on the amount of sulfur dioxide absorbed, the first partial condenser for a portion of the sulfur dioxide-water vapor may be the heat exchanger for a second stage evaporator. As the size of the chemical plant increases somewhere beyond the "production" of 5,000 lbs of sulfur dioxide the operating cost economics begin favoring a double effect evaporator. The condensers following the evaporators may be air cooled or water cooled depending on the process absolute pressure, product purity required and cooling medium available. Since a vacuum pump is required, it is proposed to cool the SO_2 product gas down as far as possible with the cooling medium and method available. The product SO_2, at least in the case of a power plant, will be used to make elemental sulfur or sulfuric acid and it is therefore advantageous to have its concentration as high as possible. Normally, this product gas will be approximately 85 volume % SO_2.

Water vapor condensed in the partial condensers contains varying small amounts of dissolved sulfur dioxide. All of this "sour" condensate is



Single Effect Evaporator Chemical Plant at the
SOCAL, El Segundo, California Installation
of the Wellman-Lord Process

The purge streams from the evaporator and purge treatment area are then combined to be further processed. The next processing step can be one of drying or neutralization. Drying of the purge will result in a marketable sodium sulfate by-product while neutralization with sulfuric acid will give a soluable waste product with a very low COD value.

THE CAT-OX DEMONSTRATION PROGRAM

ILLINOIS POWER COMPANY

THE MITRE CORPORATION

M74-106

NOVEMBER 1974

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M74-106

THE CAT-OX DEMONSTRATION PROGRAM

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Decatur, Illinois

Presented to

THE FLUE GAS DESULFURIZATION SYMPOSIUM

NOVEMBER 1974

ATLANTA, GEORGIA

Sponsored By

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ENVIRONMENTAL PROTECTION AGENCY
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NOVEMBER 1974

CONTENTS

Page

Part I--The "Cat-Ox" Project at Illinois Power 765
- 1.0 Introduction 765
- 2.0 Capital and Operating Costs 766
- 3.0 Theoretical Description 767
- 4.0 Project Timetable 769
- 5.0 Guarantee and Operating Program 770
- 6.0 Summary 771

Part II--Mitre Test Support for the "Cat-Ox" Project 774
- 1.0 Background 774
- 2.0 Program Summary 774
- 3.0 One-Year Test Program Objectives 776
- 4.0 Test Program Design 800

ABSTRACT

THE "CAT-OX" PROCESS DEMONSTRATION PROGRAM

This paper consists of two parts. Part I by W. E. Miller of Illinois Power describes the installation and step-by-step operation of the "Cat-Ox"[1] process. Part II by E. M. Jamgochian of The MITRE Corporation discusses the one-year test program which will be conducted when the Cat-Ox process is again operating.

Part I - The catalytic oxidation method developed by Monsanto Enviro-Chem Systems, Inc., for removing sulfur dioxide from flue gas of fossil fuel generating stations was installed as a prototype installation with a 15 megawatt capacity at the Portland Station of Metropolitan Edison Company in 1967. The first commercially-sized installation has been installed on the 103 megawatt Wood River #4 unit of Illinois Power Company. Although start-up and operational problems have kept the system from operating reliably, the principle of operation has been proven. The Wood River project was financed jointly by the Control Systems Laboratory of the Office of Research and Development of Federal EPA and by the Illinois Power Company.

Part II - MITRE test support for the "Cat-Ox" Demonstration Program is sponsored by the Control Systems Laboratory, Environmental Protection Agency. Status of the major task areas, and the accomplishments to date are reviewed. The areas of investigation for the one-year demonstration program are identified and the specific test objectives are discussed. The test program will evaluate process design performance, process maintainability, process availability, and process operating costs, and is designed on the basis of statistical considerations.

PART I

THE "CAT-OX" PROJECT AT ILLINOIS POWER

1.0 INTRODUCTION

In 1969, Illinois Power Company employed Battelle Memorial Institute to make a survey of research and development programs being conducted on SO_2 removal systems. After an intensive study, it appeared that the Cat-Ox System, following many years of research by Monsanto, was a feasible method and the system most nearly ready for a demonstration installation. Therefore, early in 1970, Illinois Power decided to install the first commercially-sized demonstration installation of the Cat-Ox System on the 103 megawatt Unit #4 at Wood River. This project has been jointly funded by the Federal EPA and by Illinois Power Company in an effort to advance the science of sulfur dioxide removal by developing a system which will produce a usable by-product in the form of sulfuric acid. Unit #4 at Wood River normally burns approximately 275,000 tons of coal per year with an average sulfur content of 3.1%. Based on these figures, the Cat-Ox System should produce about 25,000 tons per year of 78% concentration sulfuric acid.

Upon completion of contract negotiations, construction of the Cat-Ox System started in January, 1971, and the associated Research-Cottrell precipitator designed for Cat-Ox was completed and placed in service in February, 1972. Due to construction delays, initial start-up of the sulfur removal equipment did not occur until September 4, 1972, using natural gas for the in-line reheat burners. The System was operated for 444 hours during this period. When natural gas became unavailable, in October, 1972, it became necessary to operate the inline reheat burners on #2 oil. The reheat burners were tested with fuel oil and modified until operable during the period November, 1972 to June, 1973. The Performance Guarantee Test was satisfactorily completed using #2 oil in July, 1973. Operation in July, 1973 brought the total operating time for the "Cat-Ox" system to 602 hours. However, it was apparent to everyone involved, including Federal EPA personnel, that the continuous long-term operation of the in-line heaters on #2 oil would cause excessive contamination of the catalyst, thereby causing frequent shutdowns for catalyst cleaning. Since this would not be acceptable, it was agreed to construct an external reheat burner using #2 oil with the required heat being ducted into the System at the present location of the in-line burners. The Federal EPA, Monsanto, and Illinois Power are sharing the additional costs which now exceed $300,000 for the modification. The installation of the external burner was completed in April, 1974, and the unit was placed in operation May 7, 1974. During start-up, a leak in the lead lining of the absorbing tower was discovered. In addition, the water intake screens were plugging with debris from the Mississippi River which requires a change in design of the intake structure. It was further discovered that the impellers in the acid circulation pumps have been thermally shocked and must be replaced. These repairs and modifications have now been made and the System was placed in operation on August 14, 1974. However, additional mechanical and structural problems have since developed and the operation of the system has been sporadic.

2.0 CAPITAL AND OPERATING COSTS

The original capital costs involved in the design and construction of the Cat-Ox System were estimated at $7,300,000, including the cost of providing off-battery services. Of this amount, Illinois Power contracted to pay $3,800,000, and the Office of Research and Monitoring of the Federal EPA contracted to pay $3,500,000. Illinois Power agreed to provide the required auxiliary services, including natural gas or fuel oil for the reheat burners, cooling water for acid coolers, electric services for the induced draft fans, electrostatic precipitator, pumps, and facilities for ash disposal. Final costs are now approaching $8,500,000 resulting in an installed cost of about $84.00 per kilowatt based on the 103 megawatt net capacity of the generating unit. Of these final costs, Federal EPA will pay $3,700,000 and Illinois Power approximately $4,800,000.

Operating and maintenance costs are expected to run approximately $962,000 per year, as shown in the following tabulation:

Operating & Maintenance Cost Estimate

Operating & Maintenance Labor		$ 36,000
General Maintenance 2% x 8,000,000		$160,000
Make-up Catalyst 200,000 liters x .025 x 4 screenings per year		$ 30,000
Reheat burner fuel (burner rating 50 MM BTUH)		$534,000
Electric Power (4% of generator output)		
Capacity cost 4200 Kw x $200/Kw x .15 carrying charge	$126,000	
Energy cost 4200 Kw x 6000 hrs. x $.003 per Kwh equals $75,600. Use $76,000.	$ 76,000	$202,000
		$962,000
Possible credit for sale of acid		$200,000*

It should be emphasized that these figures do not include the cost of money or the cost of any major maintenance.

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* Assuming a $10 per ton net return.

3.0 TECHNICAL DESCRIPTION

The operation of the Cat-Ox System consists basically of the following six separate phases:

1. Fly Ash Collection
2. Conversion of SO_2 to SO_3
3. Heat Recovery
4. Removal of sulfuric acid
5. Acid mist elimination
6. Acid storage and loading

These basic steps are shown diagrammatically in Figure 1 and are described below.

1. Fly Ash Collection

The existing mechanical collector remains in service on Unit #4 to remove most of the fly ash from the flue gas. A new Research-Cottrell electrostatic precipitator with a design efficiency of 99.6% has been installed to work in series with the mechanical collector to remove essentially all the particulate matter from the flue gas. After leaving the electrostatic precipitator, the cleaned flue gas is heated and passes into the converter of the Cat-Ox System, or, during start-up or unusual operation, can be bypassed directly to the stack. The fly ash collected by the precipitators is conveyed pneumatically to the existing ash pit area. The electrostatic precipitator installation was completed in February, 1972 and has been operating with Unit #4 since that time.

2. Conversion of SO_2 to SO_3

The temperature of the flue gas leaving the electrostatic precipitator is 310°F. and is reheated to 850°F. to allow a 90% conversion of SO_2 to SO_3. It was proposed that this be done by two in-line reheat burners using natural gas or No. 2 fuel oil and by recovery of sensible heat from the treated flue gas. The reheat burners were designed to maintain the 850°F. conversion temperature regardless of boiler load. Following reheat to conversion temperature, the flue gas enters the converter where the Cat-Ox® catalyst (a vanadium pentoxide catalyst) reacts with the SO_2 to form SO_3. The converter is designed so that the catalyst bed can be emptied onto a conveyor system for transport to a screening process after which the cleaned catalyst is conveyed back to the converter. About 2.5% of the catalyst mass is lost during each cleaning process which is anticipated to occur about four times per year. About forty-eight hours is required for each catalyst cleaning.

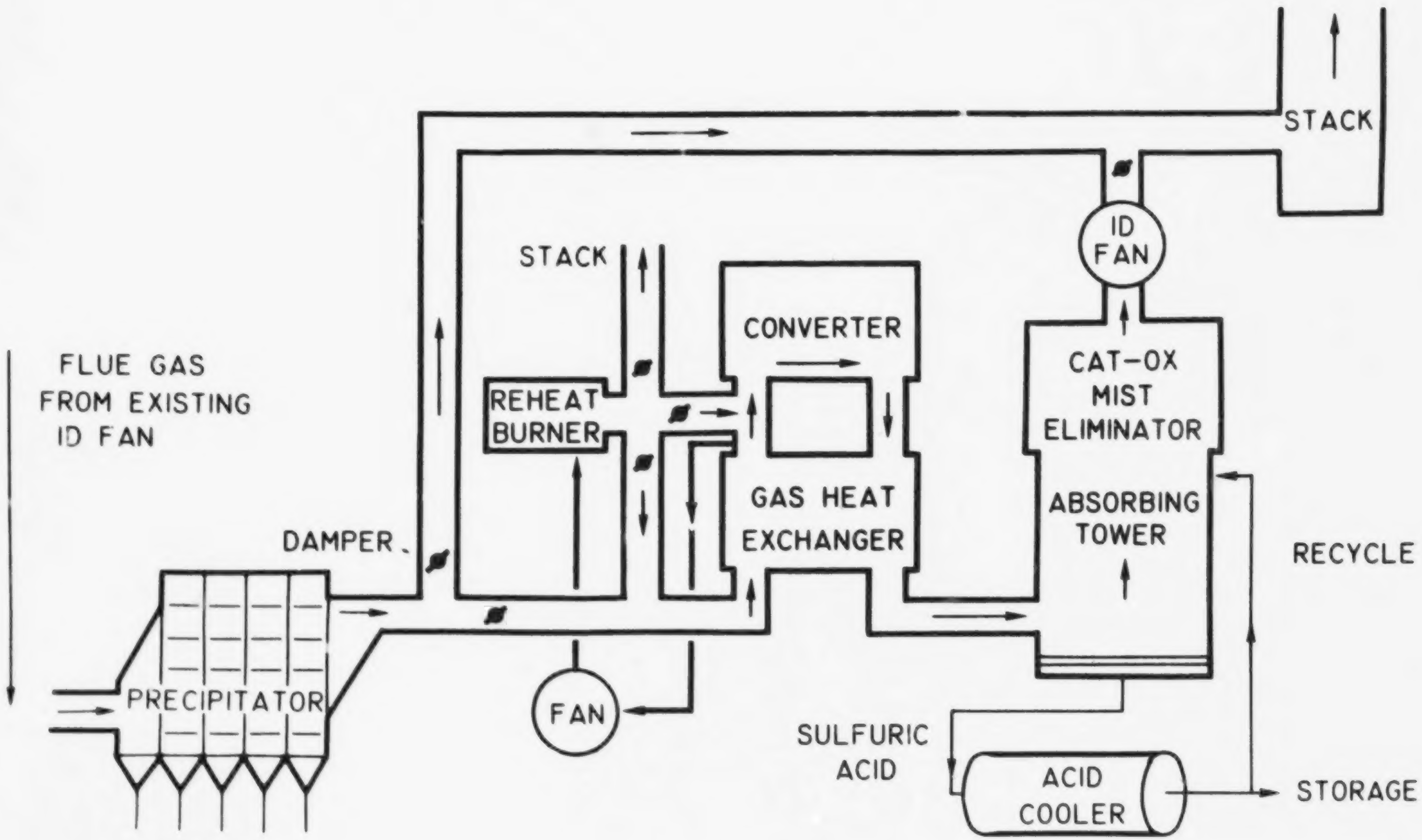
FLUE GAS
FROM EXISTING
ID FAN
PRECIPITATOR
DAMPER
REHEAT
BURNER
STACK
FAN
CONVERTER
GAS HEAT
EXCHANGER
SULFURIC
ACID
ACID
COOLER
CAT-OX
MIST
ELIMINATOR
ABSORBING
TOWER
ID
FAN
STACK
RECYCLE
STORAGE

FIGURE 1
THE REHEAT CAT-OX SYSTEM

3. Heat Recovery

The treated flue gas, now containing SO_3, passes to a Ljungstrom-type heat exchanger where about 400°F. sensible heat is recovered to heat the incoming untreated flue gas. As a result of heat recovery in this exchanger, the overall need for fuel usage is to add 150°F. of sensible heat in the Cat-Ox process. The temperature of the gas is maintained well above the dew point. Normal flue gas leakage in a regenerative heat exchanger of this type will allow about 5% of the flue gas to bypass the converter, thereby reducing the overall efficiency of SO_2 removal to approximately 85%.

4. Removal of Sulfuric Acid

The flue gas is further cooled in a packed-bed absorbing tower which operates in conjunction with an external shell and tube heat exchanger. During cooling, the H_2O and SO_3 in the flue gas combine to form sulfuric acid which condenses in the absorbing tower. The tower brings cooled sulfuric acid into direct contact with the rising hot flue gas. Exit gas leaves the packed section at about 250°F. while hot acid is constantly being removed from the bottom of the tower and cooled in the external heat exchanger and either recycled or sent to storage.

5. Acid Mist Elimination

Very fine mist particles of sulfuric acid are formed in the gas as it is cooled in the absorbing tower. These mist particles in the flue gas are removed along with some entrained droplets of circulating acid from the tower by the Cat-Ox mist eliminator system. The packed section of the absorbing tower and the mist eliminators are contained within one vessel. The flue gas leaving the mist eliminator to enter the exit stack contains less SO_3 than the amount normally emitted from the combustion process.

6. Acid Storage and Loading

The cooled acid amounting at full load to 12 gallons per minute of 78% H_2SO_4 is collected in two 400,000 gallon steel storage tanks. An acid loading pump and tank car loading facilities are provided adjacent to the storage tanks. Tank trucks may be loaded from this station if desired.

4.0 PROJECT TIMETABLE

The time schedule for the Cat-Ox System includes:

Design and Capital Cost Estimates - Initiated June, 1970

Detailed Engineering & Equipment Procurement - Initiated June, 1970

On-Site Construction - Initiated January, 1971

Electrostatic Precipitator - Placed in Operation February, 1972

Performance Guarantee Test - July, 1973

Data Phase, including 15 months operational testing by the MITRE Corporation under Federal EPA contract - estimated to be completed late 1975 or early 1976.

5.0 GUARANTEE AND OPERATING PROGRAM

The 24-hour test by Enviro-Chem was conducted to assure that the Cat-Ox System can meet the following guarantees:

1. The system is capable of operating with a gas flow of 1,120,000 #/hour entering the system at 310°F.

2. The system is capable of producing 60° Baumé (77.7% H_2SO_4) sulfuric acid.

3. The exit gas emitted to the stack does not contain, on the average, more than 1.0 milligram of 100% sulfuric acid mist per actual cubic foot of gas when the system is operated at rated capacity.

4. The conversion of SO_2 to SO_3 of the gas entering the converter shall be at least 90% of rated capacity.

5. The system shall operate so that over 99% of the fly ash in the flue gas leaving the boiler is removed when operating at rated capacity.

6. The system shall remove 85% of the SO_2 in the flue gas entering the system.

Results indicate the removal of SO_2 entering the system to be 92.1% during the period of the performance guarantee tests and 91.4% over a monitoring period exceeding 24 hours. The sulfuric acid produced was in excess of 78% concentration, the exit gas to the stack contained 0.25 - 0.53 milligrams 100% sulfuric acid mist per actual cubic foot of gas, and the fly ash removal across the Cat-Ox System alone was 99.5%.

Following repairs and modifications, the unit was started on August 14, 1974 and Illinois Power Company is attempting to operate the Cat-Ox System for a minimum of 15 months as mentioned previously. During this period, and for a subsequent period of four years, if Illinois Power Company decides to continue to operate the System, data will be obtained to evaluate the following items:

1. **Operating characteristics and plant performance (relative to SO_2 and fly ash removals and to H_2SO_4 recovery).**
2. **Maintenance procedures, requirements, and costs.**
3. **Total process operating costs.**

The photographs in Figures 2 and 3 show the Cat-Ox installation.

6.0 SUMMARY

In an attempt to advance the frontiers of knowledge in the science of removing sulfur dioxide from flue gas, Illinois Power, with Battelle Institute, conducted a comprehensive survey of possible sulfur removal systems. The possibility of using low sulfur Western coal was considered, but, in addition to increased costs, it was found to be less efficient than local coal (lower Btu, higher ash and moisture), and precipitator efficiencies declined with its use, thereby causing a violation of particulate regulations. As a result of these studies, Illinois Power Company decided that the Cat-Ox System, after both a pilot installation and prototype installation, was most nearly ready for commercial demonstration. In 1970, the capital costs being considered for Cat-Ox were much higher than those proposed for other SO_2 control systems. However, as more actual experience has been gained since 1970, it seems that the capital costs originally estimated by Enviro-Chem for Cat-Ox were more realistic than those estimated for other systems, primarily because of the decade of research and the advanced stage of development of the Cat-Ox System.

From our limited experience in operating the Cat-Ox, it is evident that the System can remove at least 85% of the sulfur dioxide from the flue gas as 78% sulfuric acid and can remove essentially all of the fly ash. Sale of the sulfuric acid may offset some of the operating costs. Illinois Power Company, by removing the pollutants from the environment and conserving natural resources by recovering a product which is presently being thrown away, is not solving one pollution problem and creating another one. While numerous start-up difficulties have been encountered with the Cat-Ox System, we are still hopeful it will prove to be a feasible method.

ACKNOWLEDGMENT

We hereby express grateful acknowledgment to the Control Sys[illegible]ns Laboratory of the Office of Research and Development of the Federa[illegible] Environmental Protection Agency for their financial assistance and [illegible] Monsanto Enviro-Chem Systems, Inc. for their technical competence.

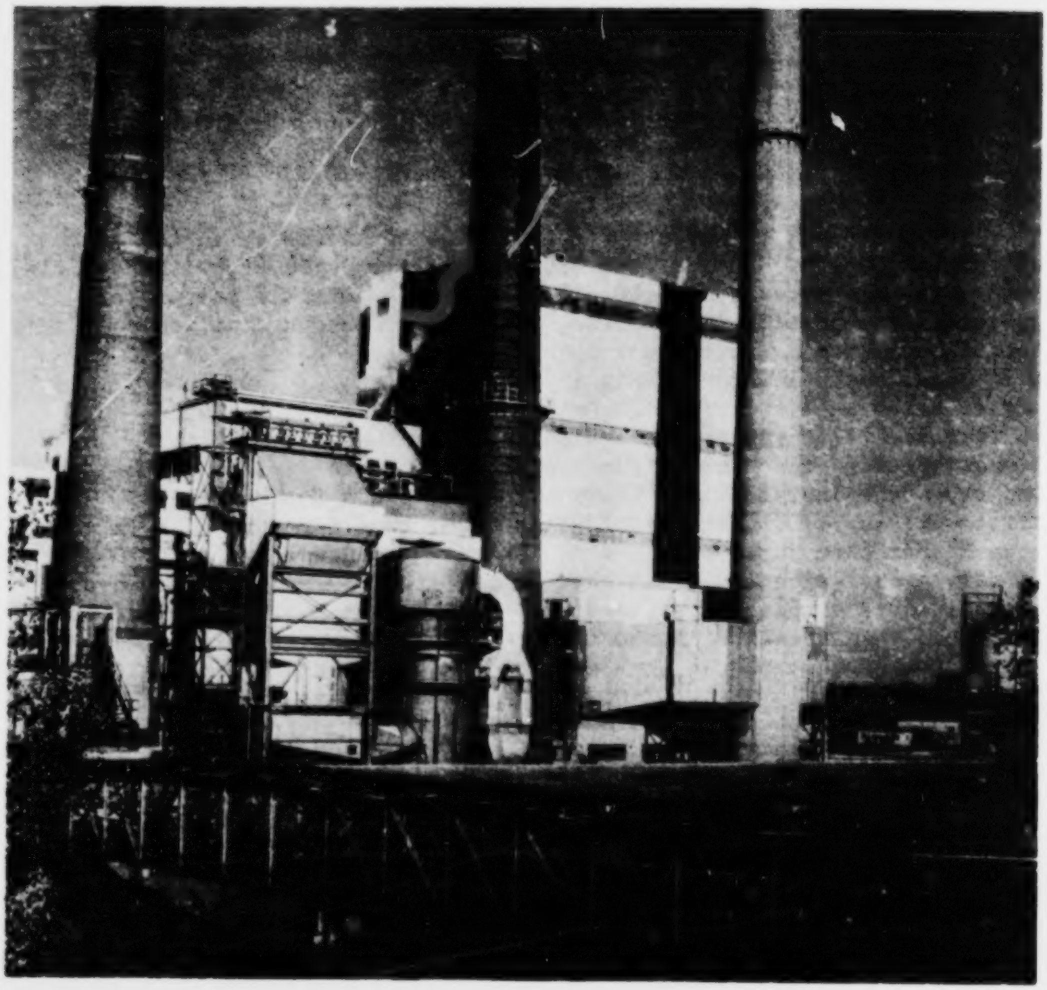

FIGURE 2
REHEAT CAT-OX PROCESS, ILLINOIS POWER, WOOD RIVER UNIT NO. 4

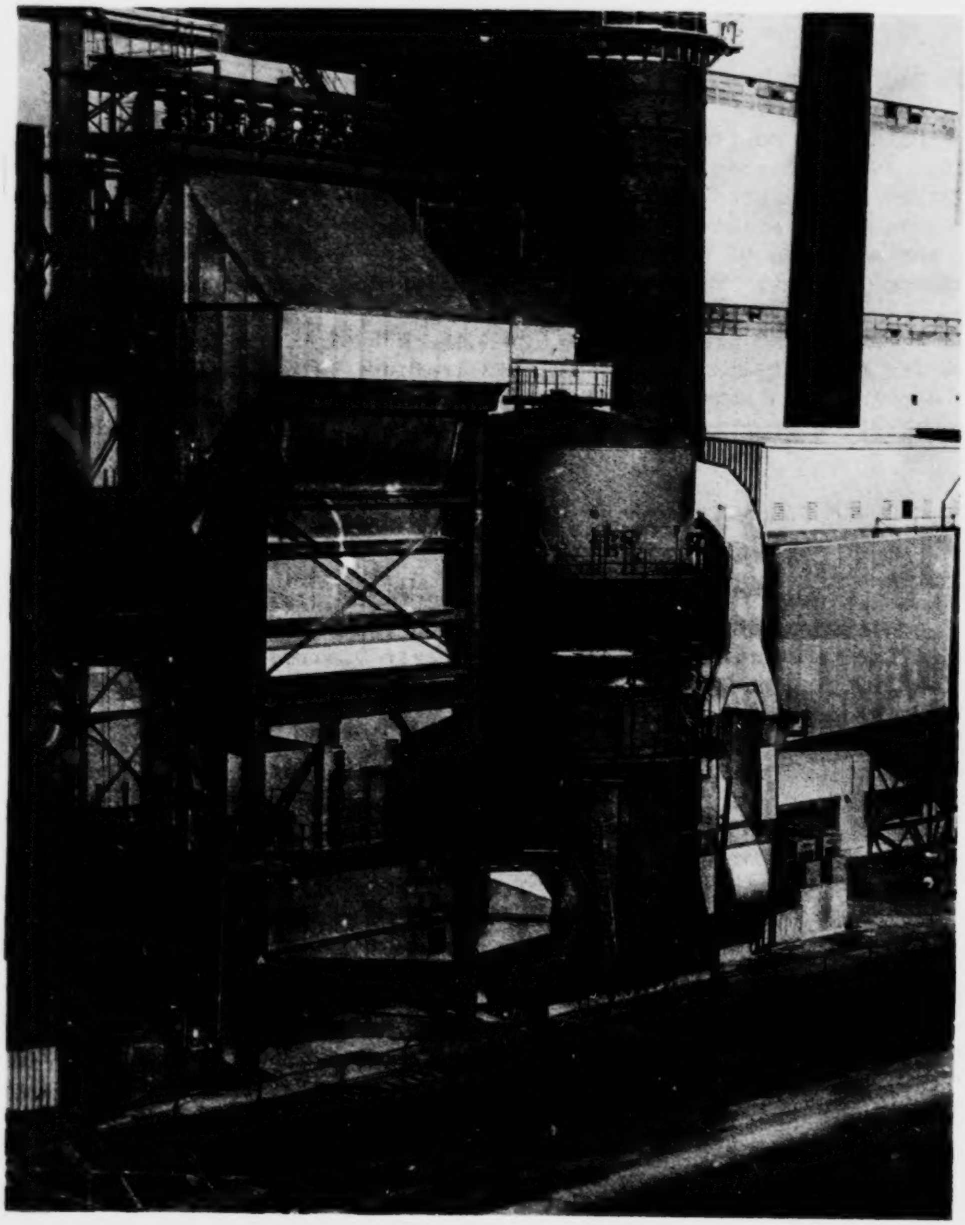

FIGURE 3
REHEAT CAT-OX INSTALLATION SHOWING CONVERTER, HEAT EXCHANGER, ABSORBING TOWER, AND MIST ELIMINATOR

PART II

MITRE TEST SUPPORT FOR THE "CAT-OX" PROJECT

1.0 BACKGROUND

MITRE was contracted by the Environmental Protection Agency in April, 1971, to provide technical support for the Cat-Ox Demonstration Program. In general, support consisted of the following: (1) program management assistance, (2) test plan development, (3) design, development, and installation of measurement systems, (4) service related to the performance of test programs, and (5) evaluation of test results.

A management plan was developed which blueprints the overall program for support of the Cat-Ox demonstration. The details of the plan are described in Management Plan for Test Support for the Cat-Ox Demonstration Program, MTR 6054, July, 1971. The major tasks defined for the program are shown in Figure 4.

2.0 PROGRAM SUMMARY

The first task area involved a definition of test requirements in which MITRE evaluated the needs of potential users and defined a set of test conditions which were reflected into the baseline measurement program. The test conditions were effectively limited in actual practice by the limiting capabilities of the Unit 4 steam generator with which the Cat-Ox process was integrated.

The second task area involved a characterization of the Unit 4 steam generator prior to installation of the Cat-Ox process with regard to operating conditions for the steam generator, flue gas properties at the steam generator/Cat-Ox process interface, pollutant emissions including SO_2 and particulates, and the evaluation of instrumentation and measurement procedures to be used during the one-year demonstration program.

The third task involves a one-year demonstration test during which a measurement program will be conducted to evaluate the Cat-Ox process control performance, process maintainability, process availability/reliability, and process operating costs. The start of this task has been delayed for approximately two years while the reheat burners of the Cat-Ox were being tested and redesigned.

In the interim, a special test program on the electrostatic precipitator (ESP) was performed to determine overall ESP efficiency and efficiency as a function of particle size. In this particular test series precipitator operating conditions were varied as well as steam generator operating conditions. In addition, specialized measurements and analyses such as in-situ resistivity, fly ash composition and gaseous SO_3 concentrations were performed to determine their effects on ESP performance. The results of these tests have been incorporated into a draft report which is currently being reviewed by EPA.

TASK 1	DEFINE TEST REQUIREMENTS	COMPLETED 1971
TASK 2	BASELINE MEASUREMENT PROGRAM	COMPLETED 1971
TASK 3	CAT-OX DEMONSTRATION	
	-PRECIPITATOR TEST PROGRAM	INTERIM TESTS 1973
	-TEST PREPARATION	COMPLETED 1974
	-ONE-YEAR MEASUREMENT PROGRAM	SEPTEMBER 1974 - AUGUST 1975
TASK 4	EVALUATION OF RESULTS	SEPTEMBER 1975 - LATE 1975 OR EARLY 1976

FIGURE 4

PROGRAM SUMMARY

At this time the Cat-Ox process is still experiencing difficulties with the redesigned reheat burners. MITRE has, therefore, initiated its test program with a block of tests on the ESP to determine if its performance has changed significantly in the past year. These tests have been completed and the results are being analyzed. It is now expected that start up of the Cat-Ox process will be initiated in late October, 1974.

The final task will be to evaluate the results of the one-year test program in terms of performance, maintainability, availability/reliability and operating costs.

3.0 ONE-YEAR TEST PROGRAM OBJECTIVES

Major areas which will be evaluated during the one-year test program are:

- Process performance
- Process maintainability
- Process availability
- Operating costs

Specific tests will be designed and performed to evaluate process performance and maintainability, whereas process availability and operating costs will be determined mostly from accurate record keeping.

Performance tests will be performed at particular periods of time to determine if the process is performing as specified. Maintainability tests will be conducted to measure changes in performance with time; to measure the effects of specified maintenance procedures and operating conditions on process performance; and to identify additional or modified maintenance procedures required to achieve design performance. Process availability will be determined by measuring the operating hours of the steam generator and the Cat-Ox process and calculating percentage availabilities relative to scheduled operation. Operating costs will take into consideration normal operational support, required maintenance, utilities for process operation, steam generator power loss due to process failure, capitalization, and by-product marketability.

Particular areas of concern are as follows:

- Operating characteristics and process performance relative to SO_2 and fly ash removal, H_2SO_4 recovery, and mist/gaseous emissions
- Response of process to fuels (varying sulfur content), load, excess air, and soot blowing
- Precipitator efficiency and outlet grain loading

- Thermal efficiency of regenerative heat exchanger and seal leakage with time
- Converter efficiency, longevity of catalyst and catalyst make-up
- Mist eliminator performance and required frequency of washing
- Corrosion rates of process materials and components

The program by which these results will be achieved is discussed in greater detail in subsequent paragraphs.

3.1 Cat-Ox Process and Measurement Locations

Figure 5 shows the flow diagram of the steam generator and the reheat Cat-Ox process. The dashed line shown in the Figure separates the steam generator from the process. The Cat-Ox process has been installed between the existing I.D. fans and the stack. The electrostatic precipitator is shown as part of the process because it is essential to the process in order to minimize contamination of the catalyst in the converter.

Flue gas from the boiler passes through the economizer and the air heater, and then enters the mechanical collector where particulates are initially removed. Particulates are further reduced to a very low level by the electrostatic precipitator. During the course of this flow the gas temperature has dropped approximately 400°F. and therefore must be reheated prior to entering the converter. Reheating of the flue gas is accomplished by the external reheat burner and the heat exchanger. The reheat burner injects heated flue gas into the main flue gas stream by means of ducts A and B at approximately 25% and 75% of the total burner output respectively. A portion of the main flue gas stream is recycled to temper the heated gas being emitted directly from the burner. This new design using an external burner replaces the original in-line burners which were not suitable for long-term operation using no. 2 fuel oil because of possible excessive catalyst contamination.

Flue gas is then ducted to the converter where the SO_2 is catalytically oxidized to SO_3. The flue gas with the SO_3 constituent is redirected to the heat exchanger so that it is cooled prior to entering the absorbing tower where the SO_3 combines with the water vapor and is absorbed into the recirculating acid. The mist eliminator removes the sulfuric acid mist which escapes from the absorbing tower with the flue gas. A second induced draft (I.D.) fan is required to make up pressure drop losses and to restore flow to the stack. Sulfuric acid from the absorbing tower and mist eliminator are pumped, cooled and recirculated through the absorbing tower. A small fraction of the total acid is periodically drawn off, cooled and pumped to the acid storage tanks.

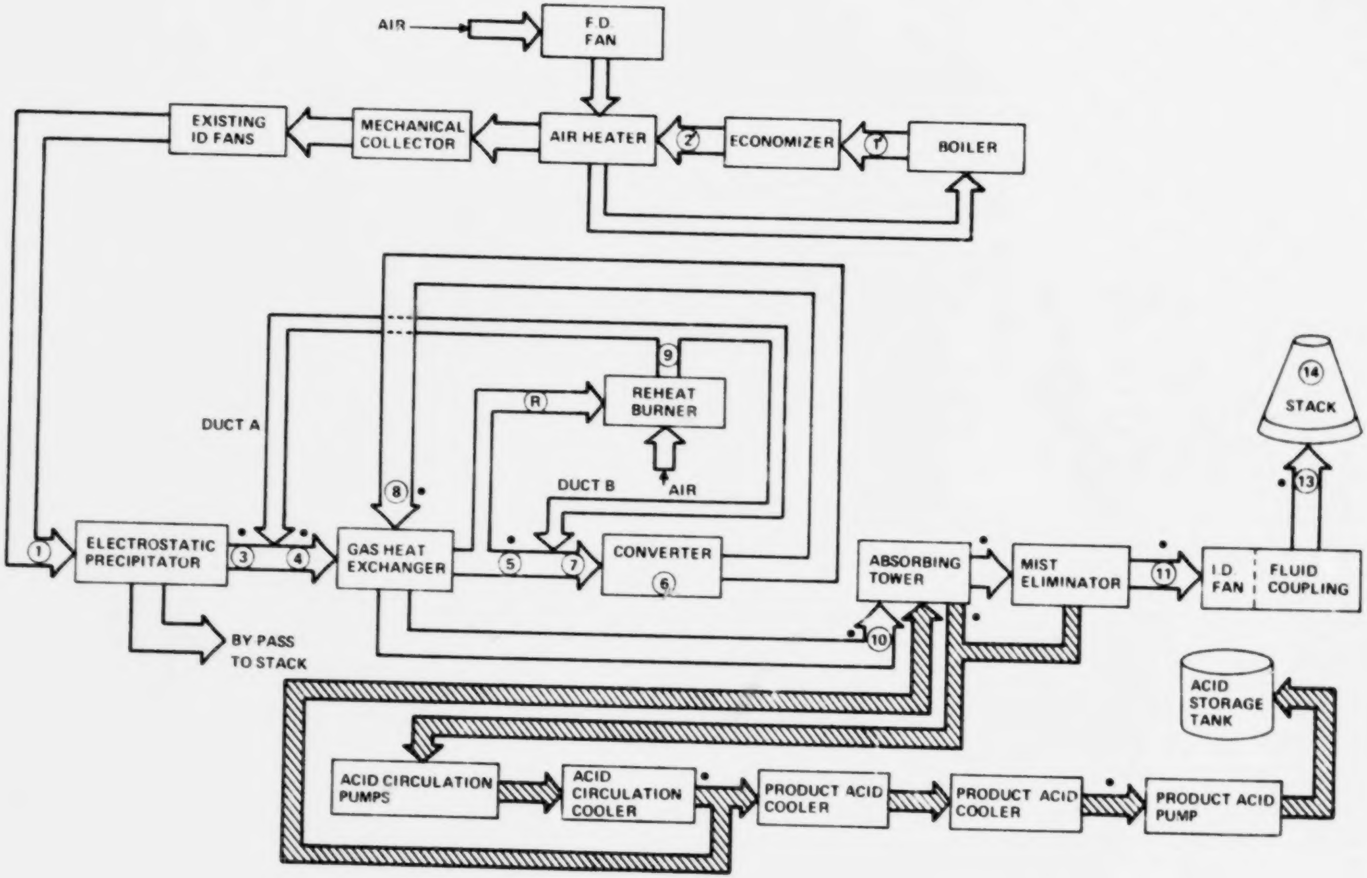
AIR
F.D. FAN
EXISTING ID FANS
MECHANICAL COLLECTOR
AIR HEATER
2
ECONOMIZER
1'
BOILER
9
REHEAT BURNER
R
DUCT A
AIR
DUCT B
14
STACK
13
8
1
ELECTROSTATIC PRECIPITATOR
3
4
GAS HEAT EXCHANGER
5
7
CONVERTER
6
ABSORBING TOWER
MIST ELIMINATOR
11
I.D. FAN
FLUID COUPLING
10
BY PASS TO STACK
ACID STORAGE TANK
ACID CIRCULATION PUMPS
ACID CIRCULATION COOLER
PRODUCT ACID COOLER
PRODUCT ACID COOLER
PRODUCT ACID PUMP

FIGURE 5
STEAM GENERATOR & CAT OX PROCESS

The numbers shown in the flow diagram identify the locations at which measurements will be made. Points 1', 2', and 14 are locations where measurements were made during the baseline program. Measurements will be repeated at these three locations to control test conditions, to permit correlation with the baseline results and to reevaluate improvements in the operational efficiency of the mechanical collector. The other measurement points identified are pertinent to evaluation of the overall Cat-Ox process and major subsystems of the process. The circular dots shown in the flow diagram identify the locations where corrosion coupons will be placed.

3.2 Discussion of Major Areas of Investigation

The Cat-Ox process has been designed to satisfy specified levels of performance for both the overall system and the major subsystems. In addition, maintenance procedures have been identified for some of the critical subsystems such as the converter. The test program which has been designed will measure the actual process performance and compare the results to the manufacturers performance specifications.

3.2.1 Design Performance Testing

Design performance testing will consist of two general areas, testing of the overall Cat-Ox process and testing of the major subsystems. The major subsystems which will be evaluated are the electrostatic precipitator, the gas heat exchanger, the converter, the absorbing tower and the mist eliminator. Where practical, testing of the overall process and various subsystems will be combined.

Figure 6 shows the test objectives of the overall Cat-Ox process with the corresponding measurement parameters and the particular measurement locations as identified previously in the process flow diagram. The measurement methods and instrumentation were reported in the Proceedings of the Flue Gas Desulfurization Symposium held in May, 1973, and will not be discussed in this paper.

Of particular interest is the overall SO_2 conversion efficiency which will be obtained by measuring the mass flow of SO_2 at the input and output of the overall process, points 1 and 14 respectively. In addition, the SO_2 contribution from the external burner will be determined by measuring the net flow, i.e., the output of the burner less the amount which is recycled. The SO_2 contribution of the external burner is extremely small. The overall process conversion efficiency is considerably influenced by the leakage of the heat exchanger which will be discussed further in this section.

The H_2SO_4 mist concentration and mass flow will be measured in the stack because this is an important pollutant, and because the process by its nature can act as an emission source. In addition, the rate of formation of sulfuric acid in the absorbing tower will be measured directly by observation of acid level as a function of time. Based

OBJECTIVE	MEASURED PARAMETERS	LOCATIONS
OVERALL SO_2 CONVERSION EFFICIENCY	MASS FLOW SO_2: GAS CONC.; GAS VOLUME FLOW	INPUT: PTS. 1, 9, R OUTPUT: PT. 14
H_2SO_4 MIST CONCENTRATION	MASS FLOW H_2SO_4 MIST/SO_3: MIST CONC.; GAS VOL. FLOW	OUTPUT: PT. 14
BY-PRODUCT GENERATION	RATE OF H_2SO_4 FORMATION: SPECIFIC GRAV., TEMP.; ACID LEVEL	ABSORBING TOWER (STORAGE TANK)
SULFUR BALANCE	MASS FLOW SO_2: GAS CONC.; GAS VOL. FLOW	INPUT: PTS. 1, 9, R
	MASS FLOW SO_3: GAS CONC.; GAS VOL. FLOW	
	RATE OF H_2SO_4 FORMATION: SPEC. GRAV., TEMP.; ACID LEVEL	OUTPUT: ABSORBING TOWER (STORAGE TANK)
	MASS FLOW SO_2, H_2SO_4 MIST/SO_3: SO_2, MIST CONC.; GAS VOL. FLOW	PT. 14
PARTICULATE REMOVAL EFFICIENCY, GRAIN LOADING & MASS FLOW RATE	MASS FLOW PART.: MASS DENSITY; GAS VOL. FLOW	INPUT: PT. 1 OUTPUT: PT. 14
GASEOUS EMISSIONS	MASS FLOW NO_2, NO_x, THC, CO_2: GAS CONC.; GAS VOL. FLOW	OUTPUT: PT. 14

FIGURE 6

OVERALL CAT-OX PROCESS PERFORMANCE

on these series of measurements which will be conducted under steady state conditions within a normal test day, a sulfur balance will be performed to check the overall accuracy of the results.

Particulate is removed from the flue gas stream prior to entering the Cat-Ox process primarily to minimize contamination of the catalyst and, therefore, to reduce the number of times the catalyst otherwise would have to be cleaned. Also, particulate collects in the heat exchanger and the mist eliminator requiring that both be periodically cleaned, and, furthermore, contaminates the sulfuric acid. Therefore, the particulate removal efficiency of the ESP is significantly important for proper functioning of the process. The particulate removal efficiency for the overall process will be higher than that for the precipitator itself because of the additional filtering inadvertently provided by the several subsystems just identified. The overall particulate removal efficiency will be measured by comparing the particulate loading in the stack to the loading at the input to the precipitator.

Finally, all the polluting gaseous emissions being emitted at the stack other than those for which the process has been designed to control will be measured. These are nitrogen oxide, nitrogen dioxide, total hydrocarbons, and carbon dioxide. In addition, oxygen and water vapor will be measured for purposes of performing necessary mass flow calculations.

Figure 7 shows the test objectives of the major subsystems. As regards the electrostatic precipitator, measurements of mass loading will be performed at the inlet (point 1) and outlet (point 3) to determine efficiency, grain loading and mass flow rate.

The heat exchanger transfers a substantial quantity of energy stored in the hot gas exiting from the converter to the lower temperature flue gas from the electrostatic precipitator. However, due to the nature of the heat exchanger design, a rotary Ljungstrom, approximately 5.2% of the flue gas leaks across the heat exchanger and is, therefore, not processed by the converter. This leakage reduces the overall process SO_2 conversion efficiency by slightly less than the amount of the leakage to approximately 85.3%. The gas leakage of the heat exchanger is specified not to exceed 5.2% provided the pressure drop from the input cold side to the output hot side does not exceed a specified level. The gas leakage will be determined by measuring the mass flow of SO_2 at the inputs and outputs of the heat exchanger. The static pressure drop will be measured at the same time to assure that it complies with specification. In addition, the mass flow of O_2 and CO_2 will be measured at the inputs and outputs to determine if there are any air leaks in the heat exchanger.

A heat balance will be performed for the heat exchanger by measuring the gas concentrations, the gas volume flow, and the temperatures of the gases at the inlets and outlets. The specific heats of the various gases will, of course, be required to perform the calculation. By applying the data on gas leakage, the thermal efficiency of the heat exchanger will be computed.

OBJECTIVE	MEASURED PARAMETERS	LOCATIONS
ELECTROSTATIC PRECIPITATOR		
PRECIPITATOR EFFICIENCY, GRAIN LOADING & MASS FLOW RATE	MASS FLOW OF PART.: GRAIN LOADING; GAS VOL. FLOW	INPUT: PT. 1 OUTPUT: PT 3
GAS HEAT EXCHANGER		
GAS LEAKAGE	MASS FLOW OF SO_2: GAS CONCS.; GAS VOL. FLOW	INPUT: PT 4, 8 OUTPUT: PT 5 + R, 10
	MASS FLOW OF O_2, CO_2: GAS CONCS; GAS VOL. FLOW	INPUT: PT 4, 8 OUTPUT: PT 5 + R, 10
	STATIC PRESSURE DROP	PT 4 - PT 10
HEAT BALANCE & THERMAL EFFICIENCY	MASS FLOW OF GAS & ENERGY: GAS CONCS. (INCL.SO_3); GAS VOL. FLOW; TEMPERATURES	INPUT: PT 4, 8 OUTPUT: PT 5 + R, 10
CONVERTER		
CONVERSION EFFICIENCY	MASS FLOW OF SO_2: GAS CONC.; GAS VOL. FLOW	INPUT: PT. 3, 4, 5, 9 OUTPUT: PT. 8
	MASS FLOW OF SO_3: GAS CONC.; GAS VOL. FLOW	INPUT: PT 5 OUTPUT: PT 8
	GAS TEMPERATURE	INPUT: PT 7 OUTPUT: PT 8
	STATIC PRESSURE DROP	PT7 - PT8

FIGURE 7

PERFORMANCE OF MAJOR SUBSYSTEMS

OBJECTIVE	MEASURED PARAMETERS	LOCATIONS
ABSORBING TOWER & MIST ELIMINATOR		
ACID FORMATION RATE & SULFUR BALANCE	MASS FLOW OF H_2SO_4 MIST/GASEOUS SO_3, SO_2: GAS CONC.; GAS VOL. FLOW	INPUT(ABSORB.): PT 10 OUTPUT (MIST ELIM.): PT 11
	ACID LEVEL VS. TIME	ABSORBING TOWER (STORAGE TANK)
	SPECIFIC GRAVITY AND TEMPERATURE OF ACID	PRODUCT ACID DISCHARGE VALVE
MIST ELIMINATOR PERFORMANCE	MIST DENSITY	OUTPUT (MIST ELIM.): PT 11
	DIFFERENTIAL PRESSURE	

FIGURE 7 (CONT'D)

PERFORMANCE OF MAJOR SUBSYSTEMS

The SO_2 conversion efficiency of the converter will be measured by determining the mass flow of SO_2 at the input and output of the converter. The mass flow of SO_2 into the converter is equal to the sum of the flows at location 5 and the contribution from the reheat burner through duct B. Because of limited number of access ports, the contribution from duct B is indirectly obtained by measuring the total SO_2 mass flow of the burner at point 9 and subtracting the fraction of the flow to duct A. The flow in duct A is obtained by measuring the difference of the flows at locations 3 and 4.

As a check on the SO_2 measurements, the mass flow of SO_3 at the input and output of the converter will also be measured. The SO_3 contribution from the external burner is expected to be negligible and will not be measured.

The temperature of the flue gas is significant as regards the SO_2 conversion efficiency and is recorded as part of the gas volume flow measurement. In addition the static pressure across the converter will be measured as an indication of fly ash accumulation and possible catalyst contamination. The design specification of the converter states that the converter efficiency is independent of fly ash accumulation.

Finally the acid formation rate of the absorbing tower will be determined by measuring acid level as a function of time. The acid concentration will be determined by measurement of specific gravity and acid temperature. In addition, the acid formation rate will be determined by measurement of the mass flow of gaseous SO_3 and SO_2 at the input to the absorbing tower and mass flow of H_2SO_4 mist/gaseous SO_3 and SO_2 at the output of the mist eliminator. The acid formation rate is determined by assuming that the difference between input to the absorbing tower and the output of the mist eliminator goes into the formation of sulfuric acid.

The mist eliminator performance will be based on the measurement of sulfuric acid mist at the output of the mist eliminator. The differential pressure f the mist eliminator will be measured simultaneously as an indication of mist eliminator operating condition.

3.2.2 Maintainability Testing

As the Cat-Ox process operates over an extended period of time, performance characteristics will change causing lower operating efficiencies and higher emission levels for the major subsystems and the overall process. The degradation in performance will be corrected at certain points in time when maintenance procedures now planned are applied to the various subsystems. Because of the lack of experience with the Cat-Ox process, the existing maintenance procedures and the frequency of application of these procedures can be expected to be modified during the course of the one-year test program. In fact, it is possible that additional maintenance procedures will be identified and applied which will permit the process to operate at best expected performance levels.

Modifications to maintenance procedures will be identified as operational experience with the process is obtained and as data is collected and evaluated.

The general objectives of maintainability testing can be stated as follows:

(1) Measure performance changes of the major subsystems and the overall Cat-Ox process with time based on an optimum statistical test design. The statistical design utilizes blocking replication and randomization to determine the major inter-relationships of boiler and process parameters while performing a minimum number of tests, thereby, minimizing test costs and interference with normal steam generator operation.

(2) Measure the effect of specified maintenance procedures and operating conditions on process performance by observing process performance before and after the application of maintenance procedures and changes in operating conditions. Measurements will be an integral part of the statistical test design and will be observed as part of the time dependent performance changes.

(3) Identify additional or modified maintenance procedures required to achieve design performance or best level of performance. Particular areas of maintenance have not been specified in the Cat-Ox design or operating manuals. Some of these areas will become better defined during the course of the test program.

Specific Objectives

The specific objectives of maintainability testing are stated in Figure 8 for each of the major subsystems. The test approach consists of several types of measurements and observations:

(1) Changes of design performance parameters with time using statistical testing.

(2) Observation of changes in operational levels of particular parameters with time.

(3) Observation of changes in mechanical and electromechanical properties of components and subsystems with time.

OBJECTIVE ELECTROSTATIC PRECIPITATOR	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
CHANGE OF EFFICIENCY & OUTPUT GRAIN LOADING VS. TIME	MASS FLOW OF PART.: GRAIN LOADING; GAS VOL. FLOW	FULL FACTORIAL TEST BLOCKS	SCHEDULED MAINTENANCE-BEFORE/AFTER
CHANGE OF ELECTRICAL CHARACTERISTICS VS. TIME	PRIMARY VOLTAGE PRIMARY CURRENT SECONDARY CURRENT	RECORDED PERIODICALLY	ADJUSTED AS REQUIRED
CHANGE OF ELECTRO-MECHANICAL CHARACTERISTICS VS. TIME	INTEGRITY OF DISCHARGE ELECTRODES OPERATION ELECTRODE VIBRATORS, FREQ. & INT. OPERATION PLATE RAPPERS, FREQ. & INT. ASH HOPPER LEVEL: INDICATORS; VIBRATORS; HEATERS	OBSERVED PERIODICALLY	ON-LINE MAINTENANCE WHEN POSSIBLE
CORROSION	MATERIALS, PT3: C-1008 C.S., 316 SS, COR-TEN TEMPERATURE, PT 3	MEASURED PERIODICALLY RECORDED PERIODICALLY	

FIGURE 8

MAINTAINABILITY TESTING

OBJECTIVE	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
EXTERNAL REHEAT BURNER			
CHANGE OF FLUE GAS TEMPERATURES VS. TIME	INPUT A: OUTLET TEMP., PT 3, 4 INPUT B: OUTLET TEMP., PT 5, 8 HEATER OUTLET TEMP.	RECORDED PERIODICALLY	MAINTENANCE OF BURNER-BEFORE/AFTER
CHANGE OF BURNER INPUTS WITH TIME	NATURAL GAS FLOW NO. 2 OIL FLOW COMBUSTION AIR FLOW AMBIENT TEMPERATURE	RECORDED PERIODICALLY	
GAS HEAT EXCHANGER			
CHANGE OF HEAT BALANCE & THERMAL EFFICIENCY WITH TIME	MASS FLOW OF GAS & ENERGY: GAS CONCS. (SO_3 INCL.) GAS VOL. FLOW; TEMPERATURES	FRACTIONAL FACTORIAL TEST BLOCKS	SOOT BLOWING-BEFORE/AFTER WASHING - BEFORE/AFTER
CHANGE OF LEAKAGE WITH TIME	MASS FLOW OF SO_2: GAS CONCS.; GAS VOL. FLOW MASS FLOW OF O_2, CO_2: GAS CONCS.; GAS VOL. FLOW STATIC PRESSURE DROP	FRACTIONAL FACTORIAL TEST BLOCKS	

FIGURE 8 (CONT.)

MAINTAINABILITY TESTING

OBJECTIVE	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
GAS HEAT EXCHANGER (CONT'D)			
CORROSION	MATERIALS, PT 4: C-1008 C.S., 316 SS, COR-TEN	MEASURED PERIODICALLY	
	TEMPERATURE, PT 4	RECORDED PERIODICALLY	
	STATIC PRESSURE, PT 4 - PT 5	RECORDED PERIODICALLY	
	MATERIALS, PT 5: C-1008 C.S., 316 SS, COR-TEN	MEASURED PERIODICALLY	
	TEMPERATURE, PT 5	RECORDED PERIODICALLY	
CONVERTER			
CONVERSION EFFICIENCY VS. TIME	MASS FLOW OF SO_2, SO_3: GAS CONC.;GAS VOL. FLOW	FRACTIONAL FACTORIAL TEST BLOCKS	CATALYST CLEANING - BEFORE/AFTER
	GAS TEMPERATURE	RECORDED CONTINUOUSLY	
	STATIC PRESSURE DROP	RECORDED CONTINUOUSLY	
STATIC PRESSURE DROP VS. TIME	CATALYST CLEANING FREQUENCY	RECORDED AS REQUIRED	
	CATALYST LOSS	RECORDED AS REQUIRED	
	DOWN TIME & MANLOADING	RECORDED AS REQUIRED	
	STATIC PRESSURE DROP	RECORDED PERIODICALLY	
	FUEL CONSUMPTION; FUEL TYPE	RECORDED PERIODICALLY	
CORROSION	MATERIALS, PT 8: C-1008 C.S., 316 SS, COR-TEN	MEASURED PERIODICALLY	
	TEMPERATURE, PT 8	RECORDED PERIODICALLY	

FIGURE 8 (CONT'D)

MAINTAINABILITY TESTING

OBJECTIVE	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
ABSORBING TOWER AND ACID LOOP			
PRODUCTION OF ACID OVER EXTENDED PERIOD OF TIME	MASS FLOW OF H_2SO_4 VAPOR, SO_2 GAS-PT 10	RANDOMIZED COMPLETE BLOCKS	CONDITION OF PACKING; LEVEL OF PACKING; CONDITION ACID DISTRIBUTOR
	ACID LEVEL OF ABSORBING TOWER	PERIODICALLY RECORDED	
	ACID LEVEL OF STORAGE TANK	PERIODICALLY RECORDED	
	SPECIFIC GRAVITY AND TEMP. OF ACID	PERIODICALLY RECORDED	
	PRESSURE DROP ACROSS ABSORBING TOWER	PERIODICALLY RECORDED	
	FUEL CONSUMPTION RATE, FUEL TYPE, LOAD LEVEL	PERIODICALLY RECORDED	
CONDITION OF ACID CIRCULATION PUMPS VS. TIME	ACID FLOW	PERIODICALLY RECORDED	
CONDITION OF ACID CIRCULATION AND PRODUCT ACID COOLERS VS. TIME	TEMP. ACID TO CIR. COOLERS	RECORDED PERIODICALLY	
	TEMP. ACID TO PRODUCT COOLER		
	TEMP. ACID FROM PRODUCT COOLER		
	TEMP. WATER TO ACID COOLERS		
	TEMP. COOLING WATER RETURN		
	PH COOLING WATER RETURN		
	TEMP. FLUE GAS FROM ABSORBING TOWER		
CONDITION OF ACID PRODUCT PUMPS VS. TIME	DISCHARGE VALVE TO STORAGE ACID LEVEL IN STORAGE TANK	RECORDED PERIODICALLY	

FIGURE 8 (CONT'D)

MAINTAINABILITY TESTING

OBJECTIVE	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
ABSORBING TOWER AND ACID LOOP (CONT'D)			
CORROSION	MATERIALS, PT 10; C-1008 C.S., 316 SS, COR-TEN, CARP. 20, ARMCO 22-13-5	MEASURED PERIODICALLY	
	TEMPERATURE, PT 10	PERIODICALLY RECORDED	
	MATERIALS, INSIDE ABSORBING TOWER:C-1008C.S., 316 SS, COR-TEN, CARP. 20, ARMSCO 22-13-5, CHEMICAL LEAD, USS T-1	AT PROCESS SHUTDOWN	
	MATERIALS, ACID FROM ABSORB. TOWER: C-1008 C.S., 316 SS, COR-TEN, CARP. 20, ARMCO 22-13-5, CHEMICAL LEAD	AT PROCESS SHUTDOWN	
	MATERIALS, ACID FROM PRODUCT COOLER: C-1008 C.S., 316 SS, COR-TEN, CARP.20, ARMCO 22-13-5, CHEMICAL LEAD	MEASURED PERIODICALLY	
MIST ELIMINATOR			
H_2SO_4 MIST DENSITY VS. TIME	H_2SO_4 MIST DENSITY - PT 11	RANDOMIZED COMPLETE BLOCKS	REPLACEMENT FIBER PACKED ELEMENTS - BEFORE/AFTER WASHING - BEFORE/AFTER

FIGURE 8 (CONT.'D)

MAINTAINABILITY TESTING

OBJECTIVE	MEASURED PARAMETERS & OBSERVATIONS	MONITORING FREQUENCY	SUBSYSTEM OPERATING STATUS
MIST ELIMINATOR (CONT'D)			
MIST ELIMINATOR WASHING	WASHING FREQUENCY: DIFFERENTIAL PRESSURE	RECORDED PERIODICALLY	
CORROSION	MATERIALS, PT. 11 C-1008 C.S., 316 SS, COR-TEN, CARP. 20, ARMCO 22-13-5, USS T-1	MEASURED PERIODICALLY	
	TEMPERATURE, PT. 11	RECORDED PERIODICALLY	
I. D. FAN			
GAS VOL. FLOW AND STATIC PRESSURE VS. TIME	GAS VOLUME FLOW: DIFF. PRES., STATIC PRES., AND TEMP. AT AVAILABLE LOCATIONS	AS AVAILABLE DURING OTHER TESTING	REQUIRED MAINTENANCE WILL BE RECORDED
	STATIC PRESSURE, PT 13 ID FAN MOTOR "A" CURRENT ID FAN MOTOR "B" CURRENT ID FAN SPEED OIL COOLER OUTLET TEMP. INBOARD BEARING TEMP. OUTBOARD BEARING TEMP. OIL SUMP TEMP.	RECORDED PERIODICALLY	

FIGURE 8 (CONT'D)

MAINTAINABILITY TESTING

Electrostatic Precipitator

The major subsystems are discussed in sequence as they appear in the process flow. The electrostatic precipitator is considered part of the process because the output grain loading will determine maintenance requirements for most of the subsystems which follow.

The most significant parameter of the precipitator is the efficiency, 99.67%, which determines the output grain loading of .005 Grains/SCF at 32°F. for an assumed input grain loading of 1.5 Grains/SCF. The efficiency and output grain loading will change with time because the electrical and electro-mechanical characteristics of the precipitator change with time. Therefore, in addition to monitoring mass flow at the input and output of the precipitator, electrical operating settings for each of the transformer test sets will be monitored for primary voltage, primary current and secondary current to observe unusual changes or gradual drifting of these parameters. These changes, if significant in magnitude, will be correlated with changes in efficiency and grain loading. In addition, any mechanical and electro-mechanical changes and failures will be noted for those cases where diagnosis is feasible. Of particular interest are the mechanical integrity of the discharge electrodes, changes in the frequency and intensity of the electrode vibrators, changes in the frequency and intensity of the plate rappers, and changes in the operation of hopper vibrators, heaters and indicators.

Electrical parameters will be manually recorded periodically and electro-mechanical/mechanical characteristics will be observed during each test.

Corrosion rates at the output of the precipitator will be measured for materials used in the construction of the process. The temperature of the flue gas will be monitored periodically for correlation with corrosion.

At the present time no regular maintenance is scheduled for the ESP. It is possible that the ESP will degrade below design performance levels and operate at a degraded level for a considerable period of time before the process is shutdown for maintenance. Degraded operation will accelerate plugging of the converter bed and may force more frequent cleaning of the catalyst. Of course, many causes of ESP degradation will be reparable on line and these will be fixed as quickly as is possible by power plant personnel.

External Reheat Burner

The temperatures of the flue gas at insertion and before/after insertion of hot gases into the main stream are important parameters for evaluating the reheat burner performance as a function of time. At the insertion point from duct A, the burner raises the temperature from 310°F. to 350°F. to prevent cold corrosion at the input to the heat exchanger. At the insertion point from duct B, after the heat exchanger, the flue gas temperature is raised from 750°F. to 850°F. at which temperature SO_2 conversion occurs efficiently. These temperatures will be recorded periodically as an indication of reheat burner performance.

In addition to flue gas temperatures, the fuel flows and combustion air flows will be monitored to determine the relationship of flue gas temperatures to energy consumption. Energy consumption will vary depending on ambient air temperatures which, therefore, will also be recorded.

The process is designed to operate over the ambient temperature range from -10°F. to 110°F. The control system of the burner will normally compensate for seasonal changes by increasing or decreasing fuel flows. These measurements will demonstrate the capability of the burner to operate over the ambient temperature range of the process.

Gas Heat Exchanger

Observations will be made of the changes in heat balance, thermal efficiency and gas leakage as a function of time using fractional factorial testing. Also a special test will be performed to check the effects of soot blowing by measuring thermal efficiency and gas leakage before and after soot blowing is performed. Soot blowing is now specified to occur at a frequency of once per week.

Washing frequency of the heat exchanger has not been specified. Observations of thermal efficiency and leakage over the period of factorial testing may indicate a desirable washing frequency. However, to assure a measure of the effect of washing, the heat exchanger will be washed during the test series and the effect on thermal efficiency and gas leakage will be observed. Washing of the heat exchanger will be selected to coincide with a time period when the process is shutdown for catalyst cleaning.

Corrosion rates will be measured at the input to the cold side of the heat exchanger and will provide a measure of the actual corrosion of the heat exchanger. Corrosion rates will also be measured at the output of the cold side of the heat exchanger where gas temperatures are higher and corrosion is expected to be lower. Temperature and static pressure will be recorded periodically at both of these locations.

Converter

Changes of conversion efficiency with time will be determined periodically on the basis of fractional factorial testing. It will be of particular interest to observe the effect of catalyst cleaning on efficiency. Therefore, fractional testing will be designed to include a measure of efficiency over one full time period including catalyst cleaning.

The temperature of the flue gas and the pressure drop across the converter will also be measured and related as conditions of converter efficiency.

Fly ash will accumulate in the converter as time progresses until the pressure drop across the converter reaches a level at which it has been specified that no further pressure build-up be allowed and that the catalyst bed be cleaned. Therefore, the pressure build-up across the catalyst will be monitored over time as a measure of the fly ash accumulation. The conversion efficiency will be plotted as a function of pressure build-up in order to verify as is specified, that conversion efficiency is independent of fly ash accumulation.

The fly ash input to the converter will also be determined by keeping a continuous record of the quantity of fuel consumed by the boiler, the type of fuel consumed, the loads at which the boiler is operated, and the operating condition of the electrostatic precipitator. The pressure drop will be plotted as a function of the integrated fly ash input to provide an indication of the rate of fly ash build-up, and to determine the approximate quantity of fuel which must be consumed before the critical pressure drop is achieved. This information could then be used to predict when the next cleaning will be required based on assumptions of fuel consumption and precipitator performance.

It is specified that cleaning of the catalyst will be required no more than once every three months on the average, and that cleaning will require 3 maintenance men for 4 shifts or a total of 96 mn-hrs. A 2.5% loss of catalyst is expected during the cleaning operation. These three conditions of catalyst cleaning, i.e., frequency, time/manhours, and catalyst loss, will be determined during each cleaning operation of the one year demonstration program. As the catalyst is delivered in 50 liter containers, the makeup loss will be determined by counting the number of 50 liter containers required to fill the catalyst bed.

The corrosion rate of several materials will be determined at the output of the converter. Despite the high concentrations of SO_3 at the output of the converter, high corrosion rates are not anticipated because of the high temperature of the flue gas.

Absorbing Tower and Acid Loop

The product acid at full load will flow at an average rate of 12 GPM and the acid level in the bottom of the absorbing tower will be maintained at approximately 24 inches. Acid flow will be measured periodically using randomized complete blocks to determine changes in flow rate with time for particular operating conditions. The rate of formation of acid will be determined indirectly by measuring the sulfur flow into the absorbing tower less the sulfur flow out of the mist eliminator as discussed previously.

Acid formation in the absorbing tower will also be measured directly using an acid level indicator. This will be accomplished by shutting off the product acid flow and allowing the acid to build up in the absorbing tower to near the alarm level. During the build-up, the acid level will be measured as a function of time. The time period of measurement will be a fraction of a test day. In addition, the acid formation in the storage tank will be measured over a longer period of time. Approximately one full test day at full load should make a measurable change in the acid level. Finally the acid level in the storage tank will be measured over an extended period of operation and will be correlated with fuel consumption, fuel type, and load.

The acid concentration will be measured once each shift on weekdays and once each day on weekends by Illinois Power personnel. The acid concentration will be determined by measurement of specific gravity and temperature.

The condition of the absorbing tower internals will be observed when feasible to ascertain the condition of the packed bed, the level of the packed bed, and the condition of the acid distributor. Inspections will be made during process shutdown, and degradations or corrections of defects will be noted for correlation with acid formation rate.

The flue gas pressure drop in the absorbing tower will be measured periodically as an indication of the status of absorbing tower internals.

The condition of the acid circulation pumps will be checked by monitoring the acid flow from the acid coolers to the absorbing tower periodically. Similarly the condition of the product acid pumps will be checked by determining acid formation rate in the storage tank as previously discussed.

The condition of the acid circulation system and product acid coolers will be monitored by periodically recording acid temperatures to the coolers and from the coolers. In addition, the temperature of the water to and from the coolers will be monitored as will the PH of the cooling water return as an indication of acid leakage. The flue gas temperature at the output of the absorbing tower will be monitored as an indirect indicator. The temperature of the flue gas is dependent on operation of the acid coolers and absorbing tower.

Corrosion rates will be determined at the flue gas input to the absorbing tower, a location where considerable corrosion has already occurred. Also corrosion rates will be determined at several locations in the acid stream, i.e., inside the absorbing tower, after the absorbing tower, to the product cooler, and from the product cooler.

Mist Eliminator

The sulfuric acid mist density at the output of the mist eliminator will be measured over an extended period of time by means of randomized complete blocks. Deterioration and replacement of fiber packed elements will be observed when possible, and noted for correlation with test data.

The pressure drop across the mist eliminator will be recorded periodically and mist eliminator washing requirements will be determined. Sulfuric acid mist density will be measured before and after washing to determine the effect of washing on mist eliminator performance.

Corrosion rates of several materials will be determined at the output of the mist eliminator.

Induced Draft Fan

The gas volume flow and the static pressures will be measured throughout the Cat-Ox process at various points during the one year test program. These measurements will indicate the performance of the induced draft (ID) fan as a function of time. In particular, the pressure at the outlet of the ID fan will be continuously monitored. In addition, motor current, fan speed, oil cooler outlet temperature, inboard bearing temperature, outboard bearing temperature and oil sump temperature will all be monitored to determine the operating condition of the I.D. fan.

Corrosion at the outlet of the ID fan will be measured and related to materials used in the fan.

3.2.3 Process Availability and Operating Costs

As yet, little is known of the operational reliability of the Cat-Ox process over an extended period of time. To obtain this information, accurate and detailed logs on the operation of both the steam generator and the Cat-Ox process will be maintained during the year long demonstration program.

The operational status of the steam generator and process and the resulting interactions will be recorded. Both the steam generator and the Cat-Ox process will operate in one of three states, that is normally, degraded or completely shutdown. Therefore, nine operating states for both the boiler and process are possible. These operating states are shown in Figure 9. Only six of the states are significant from the viewpoint of processing SO_2 in the flue gas. The other three cases are trivial because, when the boiler is out, no gas is available for processing. These six combinations resolve into three conditions, of process operation, full process availability, partial process availability and no process availability. Determination of these availability statistics are of major importance for determining the practicality of applying the Cat-Ox process.

BOILER CAT-OX	NORMAL	DEGRADED	OUT
NORMAL	Full SO_2 Processing	Full SO_2 Processing	▨
DEGRADED	Partial SO_2 Processing	Partial SO_2 Processing	▨
OUT	No SO_2 Processing	No SO_2 Processing	▨

FIGURE 9

STEAM GENERATOR/PROCESS OPERATING MODES

Data Collection and Analysis

The data which will be collected to determine process availability is shown in Figure 10. The time period of steam generator or process degradation will be recorded. The faulty subsystem/component which caused degradation or shutdown will be identified and the cause of failure will be diagnosed. Also, the recommended maintenance procedure will be recorded.

The following information will be recorded in connection with the maintenance performed:

(1) Types and number of Illinois Power personnel

(2) Subcontractor labor

(3) Man-hours by labor category

(4) Materials required

(5) Materials and labor costs and

(6) Total time required for repairs taking into account delays in assigning personnel or obtaining materials

Most of this data will be obtained from logs and records covering a full year of operation on a 24 hour/day basis. A majority of the data will, therefore, be recorded by Illinois Power in logs and records as follows:

(1) Operating Log

(2) Mechanical Maintenance Log

(3) Electrical Maintenance Log

(4) Shift Supervisors' Logs

(5) Cost Accumulation Record and

(6) Monthly Plant Managers Report

MITRE will also maintain, during its normal working day, a Test Director's Log and the recorded maintainability data discussed previously.

The data which is collected by both Illinois Power and MITRE will be analyzed to provide the following information:

(1) Total hours of steam generator/process operation in the three states of operation, normal, degraded and shutdown

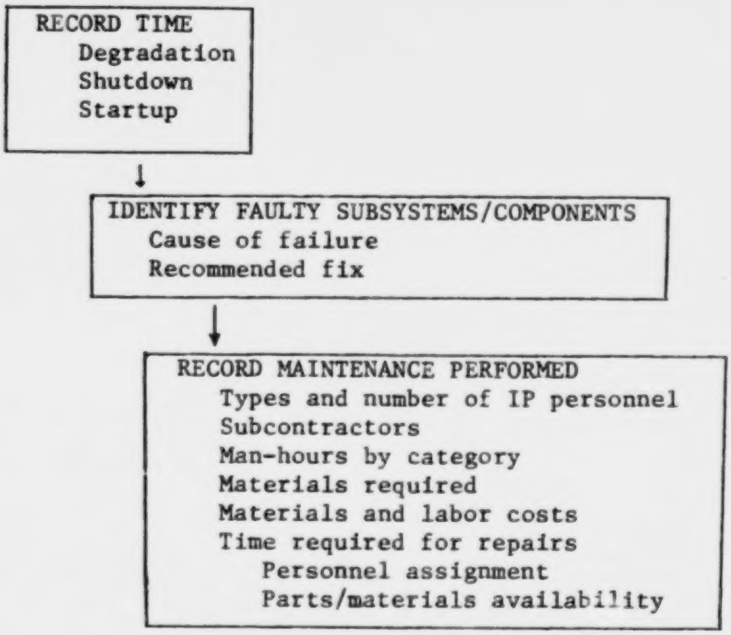
RECORD TIME
Degradation
Shutdown
Startup
IDENTIFY FAULTY SUBSYSTEMS/COMPONENTS
Cause of failure
Recommended fix
RECORD MAINTENANCE PERFORMED
Types and number of IP personnel
Subcontractors
Man-hours by category
Materials required
Materials and labor costs
Time required for repairs
Personnel assignment
Parts/materials availability

FIGURE 10

STEAM GENERATOR AND CAT-OX PROCESS AVAILABILITY

(2) Percentage availability of the steam generator and process

(3) Mean-time-to-failure of process subsystems and components for cases where sufficient data is collected.

(4) Labor categories and man-hours by category for the Cat-Ox process

(5) Significant causes of process failure

(6) Spare parts requirements for the process and

(7) Redesign requirements for the process

Evaluation of Operating Costs

The factors which will be evaluated to determine Cat-Ox process operating costs are summarized in Figure 11. Estimates of most of these factors have been made in Part I of this paper.

Normal Cat-Ox process operation will include costs of process operating personnel and the cost of borrowed money. The cost of borrowed money will reflect actual costs which would be passed on in higher rates to the consumer. Maintenance costs will include both scheduled and unscheduled maintenance, and for the most part will be collected as described previously for determination of process availability. Most of the costs for utilities will result from fuel requirements for the external reheat burner and electrical power for the process subsystems. Water treatment, cooling water, fly ash handling, and pressurized air/steam costs are expected to be small by comparison.

If the steam generator is forced to shutdown as a result of process failure, the cost of power loss will be included in the operating cost. Although the possibility of such an occurrence is not great, there is finite probability that it could occur.

Finally the quantity of acid which is generated and sold will be determined and the income received will be applied as a credit toward reducing operating costs.

4.0 TEST PROGRAM DESIGN

The design performance and maintainability tests will be performed over a range of boiler operating conditions representative of normal boiler operation. These conditions are shown in Figure 12. The minimum load was established as the lower limit achievable while consistently satisfying Illinois Power load demands. The 80 MW level was selected as the mid-point between 60 MW and 100 MW. The low load tests will generally be conducted at night when load demand is down.

- NORMAL OPERATION

    Operating personnel
    Cost of borrowed money

- MAINTENANCE (Scheduled/Unscheduled)

    Overall maintenance costs
    Personnel costs by category - mechanical, electrical
    Subcontractor costs
    Parts and Materials costs (make-up catalyst, mist eliminator wash solution)
    Overhead charges

- UTILITIES

    Fuels - external reheat burner
    Electrical power and capacity charge - all process subsystems
    Water treatment - mist eliminator wash
    Cooling water chlorination
    Fly ash handling
    Pressurized air/steam

- POWER GENERATION LOSS DUE TO PROCESS FAILURE

- MARKETABILITY OF ACID

    Quantity generated/sold
    Application/markets/transportation

FIGURE 11

EVALUATION OF OPERATING COSTS

OPERATING CONDITION	LEVEL
Load	100 MW
	80 MW
	60 MW
Fuel	3.6% wght. S Coal
	1.8% S equiv. COAL/GAS mixture
Excess Air	4.5% O_2
	4.0% O_2
	3.5% O_2
Soot Blowing	Normal
	None

FIGURE 12

STEAM GENERATOR OPERATING CONDITIONS

The fuel normally burned in the Unit 4 steam generator is a Southern Illinois coal with sulfur content of approximately 3.6% by weight. A lower level of sulfur equivalent to 1.8% S wght. will be obtained by burning a mixture of the 3.6% sulfur coal with natural gas. Natural gas is usually available during the late spring, summer, and early fall months. Low sulfur tests, therefore, will only be conducted during the early part of the program which was initiated in September and then again toward the end of the program starting around the end of April.

The majority of the tests will be conducted without soot blowing. When soot blowing is employed, the normal soot blowing cycle will be conducted including full cycling of both the wall and retractable blowers.

The range of excess air from 3.5% to 4.5% O_2 is the maximum practical for the loads which will be employed. Therefore, these conditions of excess air will be used, the two extreme levels and one at mid-point.

Because of the number of operating conditions and the several levels for each operating condition, a large number of test condition combinations are possible. It is not practical to test each subsystem for all of these combinations. Therefore, the number of operating conditions used to evaluate a particular process subsystem have been restricted to those which will significantly effect subsystem performance. Furthermore, the overall test design has been based on statistical considerations permitting the significant results to be obtained while conducting a small number of tests.

Figure 13 outlines the test program design. The program was initiated on 11 September 1974 with a block of 12 tests on the electrostatic precipitator. Precipitator performance was evaluated as a function of load, fuel and soot blowing. This first block of tests has now been completed and the data is being evaluated.

Testing of the precipitator was performed first so as to get the test program started even though the Cat-Ox process was experiencing start-up difficulties and was not yet on line. It was hoped that by the time the precipitator tests were completed the Cat-Ox process would be fully operating and the remainder of the test program could be carried out.

If gas is still available after the process does start up a special block of 4 tests will be conducted to evaluate the converter performance as a function of fuel. After which a series of 9 tests divided into 3 blocks of 3 tests each will be performed at approximately 3 week intervals to evaluate the converter and heat exchanger as a function of load and excess air, and to evaluate time dependent changes resulting from catalyst contamination and heat exchanger seal leakage. A special one day test will be performed to evaluate heat exchanger performance resulting from soot blowing of the heat exchanger. This test will be repeated again approximately 6 weeks later to verify results of the first test.

SUBSYSTEM	TIME PERIOD (WKS)	NO. OF TESTS	DESIGN	STEAM GENERATOR VARIABLES
Electrostatic Precipitator	2 1/2	12	Full Factorial	Load, fuel, soot blowing
No testing (Cat-Ox Process Start-up)	2			
Converter	2	4	Special	Fuel
Converter, Heat Exchanger		3	Frac.Fact.I	Load, Excess Air
Heat Exchanger Soot Blowing		1	Special	
No Testing	2			
Absorbing Tower	2	3	Rand. Compl. Block	Load
Heat Exchanger Soot Blowing		1	Special	
Converter, Heat Exchanger		3	Frac.Fact.II	Load, Excess Air
No Testing	2			
Mist Eliminator Wash	1	1	Special	
Absorbing Tower		3	Rand.Compl. Block	Load
Converter, Heat Exchanger	1	3	Frac.Fact.III	Load, Excess Air
No Testing - Steam Generator and Cat-Ox Process Maintenance (Catalyst cleaning, H.E. Wash)	5			
Converter, Heat Exchanger	2	3	Frac.Fact.I'	Load, Excess Air
Mist Eliminator Wash		1	Special	
Absorbing Tower		3	Rand.Compl. Block	Load
No Testing	2			
Mechanical Collector, Precipitator and Overall System (Part.)	1	3	Special	Load

FIGURE 13

SUMMARY OF TEST PROGRAM DESIGN

SUBSYSTEM	TIME PERIOD (WKS)	NO. OF TESTS	DESIGN	STEAM GENERATOR VARIABLES
Converter, Heat Exchanger	1	3	Frac.Fact. II'	Load, Excess Air
No Testing	3			
Converter, Heat Exchanger	1	3	Frac.Fact.III'	Load, Excess Air
No Testing	2			
Overall System	1 1/2	6	Frac.Fact.I	Load, Fuel,Excess Air
No Testing	2 1/2			
Overall System	2	6	Frac.Fact.II	Load, Fuel,Excess Air
No Testing	2			
Overall System	1 1/2	6	Frac.Fact.III	Load, Fuel, Excess Air

FIGURE 13

SUMMARY OF TEST PROGRAM DESIGN (CONT.'D)

The absorbing tower performance will be evaluated as a function of load only. Subsequently a second block of the same tests will be repeated three weeks later to observe time dependent changes which may have occurred and provide needed replicates. A special one day test will be performed to evaluate the effects of mist eliminator washing.

A scheduled outage of the steam generator and Cat-Ox process is planned during January, 1975. During this outage, maintenance will be performed on both the steam generator and the Cat-Ox process. In particular, the catalyst in the converter will be cleaned and the heat exchanger will be washed. The effect of these two maintenance procedures will be measured by performing a second series of tests on the converter and heat exchanger consisting of a series of 9 tests in 3 blocks of 3 tests each. In addition, the absorbing tower tests will be repeated a third time to observe any improvement which may have resulted from maintenance performed on the absorbing tower.

A special block of tests will be performed to determine the efficiency of the mechanical collector, any changes in performance of the precipitator since the start of the program, and the overall Cat-Ox process particulate removal efficiency.

The final series of tests will involve the overall system performance as a function of load, fuel and excess air. This series will consist of 18 tests divided into 3 blocks of 6 tests each separated by approximately 2 weeks to obtain time dependent changes on the overall process performance.

ACKNOWLEDGEMENT

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1. Proprietary term and registered trademark of Monsanto Enviro-Chem Systems, Inc.

The Shell Flue Gas Desulfurization Process

by

J. B. Pohlenz
UOP Process Division
Universal Oil Products Company
Des Plaines, Illinois

For presentation at the
Environmental Protection Agency
Flue Gas Desulfurization Symposium
Atlanta, Georgia, November 4-7, 1974

THE SHELL FLUE GAS DESULFURIZATION PROCESS

by J. B. Pohlenz
UOP Process Division
Universal Oil Products Company
Des Plaines, Illinois

MECHANISM OF SO_2 CAPTURE AND RELEASE

In the early 1960's Shell (Shell International Petroleum) initiated a development program to separate SO_2 from flue gas containing, along with the usual products of combustion, oxygen and particulate matter. It was the objective that the process should utilize a dry, selective adsorbent to avoid the complications often characteristic of "wet" systems and that the energy requirements to achieve isolation would represent but a modest fraction of the energy transfer being effected by the flue gas generator being serviced. A number of metal oxides have the desired thermodynamic properties but, to be used effectively, must be displayed with porous supports and, since the properties of supported systems cannot be predicted from those of pure compounds, a number of supported metal oxides were experimentally investigated to determine which, if any, would show a high reactivity with SO_2 to the metal sulfate and which could be regenerated at the same temperature to release the sulfur as SO_2.

It was found that cupric oxide had outstanding properties for such an application in that CuO readily reacts with SO_2 in the presence of oxygen at temperatures around 400°C to yield

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$CuSO_4$, which can be easily reduced at the same temperature to yield the sulfur as SO_2; further, $CuSO_4$ is stable to thermal dissociation at the acceptance/regeneration temperature.

In the selection of the acceptor support, the requirements to be met are adequate acceptance and regeneration rates coupled with chemical and physical stability. Activated alumina is the preferred carrier but is attacked by SO_3, forming $Al_2(SO_4)_3$, which creates strains in and weakens the alumina structure. But by applying stabilizing techniques to the alumina during manufacture of the catalyst, avoiding excessive temperatures in the processing cycle and maintaining good regeneration procedures, the acceptor support does not disintegrate in use.

Effective exposure of the acceptor material to the flue gas can be achieved with conventional reactor designs employing moving packed beds, fixed packed beds, or fluid systems. Reactor designs with moving solids have the advantage of providing continuous processing but have the disadvantage of acceptor attrition, particulate matter separation and relatively complex solids-handling operations. This leaves a fixed, packed bed as possessing the most suitable characteristics. However, it is not applicable in its usual form since pressure drop would be excessive and plugging with particulate matter would be unavoidable. A new fixed-bed reactor design was developed in which the flue gas flows through open channels alongside and in contact with the acceptor material. With this design, pressure drop is low, soot and fly ash pass through the channels without causing plugging, and the CuO is so effectively presented to the SO_2 in the flowing gas that capture is completed in less than one-half second.

Summarizing, a process has been developed employing a dry acceptor, CuO on alumina in a fixed, packed bed, to extract sulfur oxides from flue gas containing oxygen and particulate matter. As the acceptor becomes loaded with sulfur, the desulfurization efficiency decreases, and the material is regenerated in-situ and at the same temperature to release the sulfur as sulfur dioxide in the regeneration off-gas. Two or more identical reactors are applied in swing operation to provide for continuous processing of flue gas. The SO_2 in the off-gas from regeneration, free from oxygen and particulate matter, can be processed to yield liquid SO_2 or elemental sulfur.

Stoichiometry

The stoichiometry of the three reaction steps - oxidation, acceptance, regeneration - serves not only as a convenient summarization but can also provide a quantitative measure for reaction efficiency. The copper in the regenerated acceptor exists primarily as elemental copper with small quantities as cuprous sulfide (Cu_2S). Upon contact with oxygen in the flue gas, the copper and Cu_2S react rapidly to form CuO and $CuSO_4$:

$$Cu + 1/2\ O_2 \longrightarrow CuO$$

$$Cu_2S + 5/2\ O_2 \longrightarrow CuO + CuSO_4$$

Thus, the formation of Cu_2S is undesirable since, on subsequent oxidation, one-half of the copper in this form is converted to $CuSO_4$ and is unavailable to participate in the acceptance reaction:

$$CuO + 1/2\ O_2 + SO_2 \longrightarrow CuSO_4$$

The SO_2 is reacted until the conversion of the CuO to $CuSO_4$ has proceeded to such an extent that the unconverted CuO has been reduced to a low concentration level; the amount of SO_2 which escapes capture reaches the maximum acceptable and the partially loaded acceptor is regenerated. This acceptance reaction is shown graphically in Fig. 1(6), expressing the SO_2 content of the treated gas as a function of elapsed time after flue gas is contacted with regenerated acceptor. The SO_2 "spike" at the beginning of the cycle represents the SO_2 slippage which occurs during the first few minutes while the copper is converted to cupric oxide. If the acceptance is continued past 120 minutes, the concavity of the curve reverses and SO_2 content of the treated gas approaches that of the feed asymptotically.

Thus, at practical levels of desulfurization, a portion of the copper exists as CuO when the acceptor is regenerated -

$$CuO + H_2 \longrightarrow Cu = H_2O$$

$$CuSO_4 + 2\ H_2 \longrightarrow Cu + SO_2 + 2\ H_2O$$

The efficiency of copper utilization can be expressed in terms of two parameters which, in turn, can appear in the stoichiometric coefficients of the reaction cycle:

Basis: 1 Mole Cu

$$\text{Let } \alpha = \frac{Cu}{Cu + 2\ Cu_2S}\text{, after regeneration}$$

$$\beta = \frac{CuSO_4}{CuSO_4 + CuO}\text{, after acceptance}$$

OXIDATION:

$$\alpha\ Cu + \left(\frac{1-\alpha}{2}\right) Cu_2S + \left(\frac{5-3\alpha}{4}\right) O_2 \longrightarrow \left(\frac{1+\alpha}{2}\right) CuO + \left(\frac{1-\alpha}{2}\right) CuSO_4$$

ACCEPTANCE:

$$\left(\beta - \frac{1-\alpha}{2}\right) CuO + \left(\beta - \frac{1-\alpha}{2}\right) SO_2 + 1/2 \left(\beta - \frac{1-\alpha}{2}\right) O_2 \longrightarrow \left(\beta - \frac{1-\alpha}{2}\right) CuSO_4$$

REGENERATION:

$$\beta CuSO_4 + (1-\beta)\ CuO + (\beta - \alpha + 2)\ H_2 \longrightarrow \alpha\ Cu + \left(\frac{1-\alpha}{2}\right) Cu_2S + \left(\beta - \frac{1-\alpha}{2}\right) SO_2 + (\beta - \alpha + 2)\ H_2O$$

The hydrogen required per unit of SO_2 removed and released can be expressed in the mole ratio -

$$\frac{H_2}{SO_2} = \frac{(\beta - \alpha + 2)}{\left(\beta - \frac{1 - \alpha}{2}\right)}$$

The minimum requirement is that for which all the copper is present as $CuSO_4$ going into regeneration and all the copper is present as elemental after regeneration. In this event $\beta = \alpha = 1$ and the H_2/SO_2 is 2.0. The characteristics of acceptor material produced in commercial quantities is such that values of β commonly range from 0.7 - 1.0 depending on operating temperature, gas velocity and sulfur removal required. A combination of acceptor improvements and operating techniques almost totally suppress cuprous sulfide formation so that real hydrogen requirements exceed theoretical by only 10-25%.

Copper sulfate releases the accepted sulfur in the form of SO_2 upon regeneration with reducing agents such as H_2, CO, and light hydrocarbons at temperatures of approximately 400°C. The rate of regeneration with various regenerants has been investigated and reported (1); from this work it was determined that hydrogen has economic advantages due to its high reactivity with copper sulfate; in fact, at temperatures above 300°C, the reduction of $CuSO_4$ is limited by the supply rate of hydrogen. The regeneration reaction is illustrated graphically in Fig. 2(5) which shows the sulfur release rate against cumulative time after regeneration commences.

DEMONSTRATION UNIT - SHELL'S REFINERY IN PERNIS

After extensive bench scale testing to define reaction mechanism, kinetics and acceptor performance, a demonstration unit was erected in 1967 in the Shell Refinery near Rotterdam. The design of the unit was based on a kinetic model of the parallel passage system and the concept of unit cells, a basic module for containing the acceptor was first introduced. The nature of the process permits such an approach, since any size of reactor can be based on a unit cell of internals, each containing a series of acceptor layers and gas channels. The cross-sectional area of the cell fixes the volumetric rate of gas processed per cell; the height (number of cells stacked in series) fixes the extent of desulfurization and sulfur-holding capacity. An adiabatic reactor containing a single stack of unit cells operates under the same restraints of heat flow, temperature and composition profiles, space time and contact time as if it were in parallel with many other identical cell-stacks. Thus, scale-up to commercial size can be accomplished in a single step.

In the Pernis unit, 400-600 scf/minute (600-1000 Nm^3/h) of flue gas containing 0.1- 0.3 vol. % SO_2 was isokinetically sampled from the main flue gas duct of a process heater fired with heavy, high-sulfur fuel oil. The flue gas was drawn through the reactor at 350-450°C by means of a steam ejector, and the treated gas was returned to the main flue gas duct of the furnace. The reactor normally contained 3.5 cu. ft. (0.1 m^3) of acceptor. The acceptance time was varied between 0.5 and 2 hours in order to arrive at an SO_2 removal efficiency of about 90% for gases with various contents of SO_2. The regeneration of the acceptor was carried out in a time equal to or shorter than the acceptance time. The unit is fully automated and runs unattended.

During the approximately 20,000 operating hours of the Pernis unit a great number of tests were run with various regeneration agents, with different types of copper-on-alumina acceptor of varying copper content, and with a number of different construction materials for the reactor internals.

The results of these tests are summarized below (6):

- Diluted hydrogen-containing gases are preferred as regeneration gas.
- An acceptor based on a stabilized alumina support will have a life in excess of 8000 cycles (i.e., in excess of 1.5 years' service life). The acceptor is resistant to chemical and mechanical attrition; no fines will be formed or copper lost.
- The many chemical species present in the flue gases originating from firing a variety of fuels (gas up to and including heavy

asphalt) do not affect the physical and chemical stability of the acceptor.

- The pressure drop over the reactor was low and remained constant during all life-testing runs. A typical value for the particulate content of the flue gas passing through the reactor is 0.12 grains/scf (300 mg/Nm^3) when firing long residue. This value increases sharply during soot-blowing.
- Corrosion rates for a number of metals under SFGD reactor conditions have been established. With the proper materials of construction service life of the reactor internals has been estimated to exceed 15 years.

COMMERCIAL UNIT AT SHOWA YOKKAICHI SEKIYU (SYS)

The SFGD unit at SYS was designed to effect 90% desulfurization on 125,000 Nm^3/hr. of flue gas containing 2500 ppm of SO_2; this was the combined flow of flue gas from an oil-fired boiler and incinerated tail gas from a Claus unit. Between design and start-up, the Claus unit had been permanently shut down so that the SFGD unit processed only flue gas from the boiler. The SO_2 in the regeneration off-gas is reduced to elemental sulfur in a second Claus unit located approximately 1 kilometer away and its tail gas is processed elsewhere. Design and actual sulfur loads are shown in Fig. 3. A simplified process flow diagram is shown in Fig. 4; a photograph of the reactors is in Fig. 5.

The reactor section consists of two identical, parallel-passage reactors, each containing 68 cell-stacks. The regeneration of the spent acceptor is carried out with a diluted hydrogen stream producing off-gas at an intermittent rate and containing SO_2, water vapor, unconverted regeneration gas and whatever inerts are present with the hydrogen. The SO_2 is co-processed in a Claus unit with normal refinery acid gas streams and, in order not to suppress the Claus conversion by flow fluctuations, water vapor and inerts, the SO_2 present in the regeneration off-gas is isolated in an absorber-stripper system. The flow fluctuations of the stripper overhead are damped by incorporating surge capacity in the bottom of the absorber.

Two features of the process received special attention: The flue gas valves which serve to isolate the reactors from flue gas during regeneration and the unit cells in which the acceptor is held in gauze envelopes in such a way as to meet the requirements of the parallel passage design. The valves selected are a special flapper-type design with good sealing characteristics manufactured by Gebr. Adams, Bochum, Germany. After some modifications, this valve has been subjected in a special test rig at Shell's Pernis Refinery to over 40,000 cycles (approx. 8 years' operation) at 450°C using steam as the test gas. It was found that this design would meet the specifications. Commercialization of the manufacture of unit cells was achieved by Nihon Mesh Co. (Tokyo) with the assistance of Japan Gasoline Co. (Tokyo), after a number of trials to meet the rather stringent tolerances. Both cells and valves are available from fabricators in the U.S.A.

The acceptor was developed by Shell at its Amsterdam laboratories and the successful translation to commercial production was completed by Ketjen Catalyst, AKZO Chemie B.V., Amsterdam, who supplied the acceptor loading for the SYS unit.

Operating Experience at SYS (5)

The SYS unit was successfully started in August 1973 and, except for acceptor life, had successfully completed its test runs by Sept. 10, 1973. The main operating data are summarized in Table I and show that the performance of the reactor section was as expected: an overall SO_2 removal efficiency of 90% and a hydrogen consumption of about 0.2 wt-% H_2/wt-% S recovered.

A close match was obtained between the predicted and measured SO_2 concentrations in the treated flue gas (Fig. 1) and the predicted and measured SO_2 release during regeneration (Fig. 2) These operating results indicate that:

- The commercial acceptor has the required and expected SO_2 removal activity and capacity.
- The computer programs developed to simulate the performance of commercial units provide a useful means for reactor design and design optimization.
- Engineering scale-up from the Pernis demonstration unit size (600 Nm^3/h) to the SYS reactor size (125,000 Nm^3/h) or any other size consists, apart from paying attention to flow distribution and mechanical requirements for which the scale-up principles are known, simply of the parallel installation of standardized unit cells. The Pernis unit has one unit cell in a horizontal reactor cross-section, whereas the reactors in the SYS unit have 68 identical (larger) unit cells in a cross-section.

The experience gained with the special features incorporated in the reactor section is as follows:

- The unit cells were easy to handle and easy to load into the reactors.
- The automatic sequence controller operates the unit by setting the duration of the acceptance and regeneration cycles and by

continuous checking of all important valve positions, flows and temperatures. The required attention of operators, after the start-up and the initial operation period, was reduced to almost nil. No extra manpower is required to operate this unit.

- The special, large flue gas valves are working satisfactorily, as are all other sequence-controlled valves (wedge-in-wedge type).
- The pressure drop over the reactors is low (8.6 inches WG) but somewhat higher than expected (6 inches WG).
- The "open bypass" (continuous recycle of a small quantity of treated flue gas) effectively prevents any pressure surges caused by reactor switching from influencing the boiler operation.

After some initial problems in the work-up section had been remedied, the absorber efficiency is 99.9% and the total sulfur content of the stripped water is about 20 wt.-ppm S, of which 75% is present as sulfate. The co-processing of the SO_2 in the Claus unit has no effect on the efficiency of this unit.

During the first year, the only significant operating problem requiring adjustment in processing conditions resulted from partial condensation of the steam used to purge the reactor before and after regeneration. Since this purge steam flow is intermittent, somewhat more than the usual attention to engineering detail is required to avoid excessive loss of superheat temperature and subsequent formation of liquid water.

SFGD for Coal-Fired Boilers

Flue gas from oil-fired boilers normally contains 0.02-0.12 gram/SCF (50-300 mg/Nm^3) of solid material. Coal-fired boilers, however, produce off-gas with solids contents which may be higher by a factor of 50 to 100. Moreover, the solids compositions differ considerably, and components might be present which have an unfavorable effect on the performance of the copper acceptor. Thus, a sound program on coal-fired systems must demonstrate (1) the ability of the cell design to operated in a stable manner with very high loadings of particulate matter and (2) the chemical and physical stability of the acceptor material.

Accordingly, a two-phase program has been devised, the first phase comprising continuous operation of a relatively simple dummy reactor set-up with no acceptance/regeneration cycle. The second phase is the demonstration of the actual performance of the acceptance/regeneration system.

Test - Coal-Fired Utility Boiler in Rotterdam

For the first phase a dummy parallel-passage reactor was erected next to a coal-fired 57 MW B & W utility boiler of the "Galileistraat" Power Station of the Gemeente Energiebedrijf, Rotterdam, The Netherlands.

In these tests a slip stream of flue gas upstream of the air preheater and the precipitator was isokinetically sampled from the main duct and drawn through a parallel-passage reactor by means of a steam ejector. The unit was further provided with a heater to ensure a constant reactor inlet temperature of 400°C, a cyclone and filter assembly to measure actual particulate content of the flue gas at the inlet and the outlet of the reactor, and facilities for measuring erosion/corrosion of various materials at different gas velocities.

With particulate matter loadings of 2-4 gr/SCF (6-9 g/Nm^3) and peak concentrations of 8 gr/SCF during soot blowing, the dummy reactor set-up was first tested for 120 hours under typical SFGD reactor conditions to determine the resistance of the parallel-passage system to fouling by the unfiltered flue gases. Over that period no increase in pressure drop was observed, nor did visual inspection show any signs of deposits interfering with the process.

In a second test, the unit was subjected to continuous operation for 703 hours at a flue gas velocity of twice the velocity normally experienced in the SFGD process, so as to provide erosion/corrosion rate data for engineering design aspects.

In this second 703-hour test, the reactor had been filled with copper-on-alumina acceptor which, therefore, has been subjected to the rather severe conditions of continued acceptance during 703 hours. Measurement of the performance of the acceptor in laboratory apparatus after this test showed that the acceptor stability was equivalent to that of acceptor from life tests in the oil-fired Pernis demonstration unit.

This work demonstrated the effectiveness of the parallel passage principle to cope with high particulate loadings from a coal-fired utility boiler and suggested that the system could function successfully through oxidation-reduction cycles.

Demonstration Unit at Tampa Electric Company

The SFGD unit is fitted to process a slip stream from units 1 or 2 of TECO's Big Bend Station. These units are fired with predominantly Western Kentucky coal, have a design rating of 446 MW, and were designed and constructed by Stone and Webster. Flue gas is withdrawn upstream or downstream of the cold precipitators at a temperature of approximately 275°F.

A simplified process flow of the SFGD system is shown in Fig. 6.

The single reactor contains a stack of up to 5 unit-cells or modules which are identical with those in the SYS unit. The flue gas capacity per stack of unit cells is approximately the flue gas output of 0.6 megawatt, and the desulfurization capacity per stack is that which will provide 45-60 minutes of operating time and achieve 90% desulfurization of a flue gas containing approximately 3000 ppm of SO_2. The hydrogen used to regenerate the acceptor is drawn from a portable hydrogen trailer and is diluted before use. The reactor is purged before and after regeneration with superheated steam; the regeneration off-gas is returned to the main flue gas duct.

An SFGD unit may be applied to a boiler in two ways: (1) integration between the economizer and air preheater to reduce the temperature adjustment required for the acceptance reaction and (2) add-on downstream of the air preheater, requiring additional fuel to increase the gas temperature to 700°F and heat exchange to recover some portion of the added thermal energy. As a practical matter, the net re-heat requirement for the add-on application is approximately 35°F of semsible heat on the flue gas, equivalent to 1% of the fuel input to the boiler.

Since the SFGD process removes SO_3 as well as SO_2, integration between the economizer and air preheater permits greater heat recovery in the air preheater due to the decrease in the sulfric acid dew point. When burning high sulfur fuels, this depression of acid dew point will allow a reduction of flue gas temperature as much as 70°F, equivalent to 2% of the fuel input to the boiler.

The demonstration unit has been designed as an add-on retrofit. A regenerative heat exchanger reduces the fuel requirement to the in-line heater to raise the flue gas to the temperature required for good acceptor utilization, 700-800°F. The blower is oversized so that the gas rate to the SFGD unit is held constant with the excess by-passing the reactor. The valves and sequence controller are similar to those used in the SYS design. SO_2 content of the flue gas in and out of the reactor, as well as in the regeneration off-gas, is monitored automatically with infrared analyzers.

The test program originally planned for the SFGD unit at TECO called for approximately 90% desulfurization on 1200-1400 scfm of flue gas carried out over several thousands of cycles to clearly establish physical and chemical stability. However, since the plant is well instrumented, the test program has been modified to allow for a process variable study while the acceptor life-test is in progress. This will permit a direct comparison of the performance of the same acceptor material at SYS and TECO.

The acceptor activity/stability test, which is in progress, will span 5000 cycles (equivalent to 20,000 hrs. operation at SYS) of which 500 cycles will be on flue gas taken up-stream of the precipitator. During this life-testing, a series of tests of short duration is being performed in order to observe the following:

1. The effect of gas velocity on the desulfurization efficiency and reactor pressure drop.
2. The effect of acceptance time on slip curves at 75-90% desulfurization.
3. The effect of flue gas inlet temperature on removal efficiency at various gas velocities and on regeneration efficiency.
4. The effect of reactor length on desulfurization efficiency and pressure drop.

The reactor will be opened after 3000 and 5000 cycles to obtain samples of acceptor for laboratory evaluation and to determine erosion and corrosion rates of the unit cells. Also at suitable intervals, the gas streams will be analyzed for solids, SO_3 and H_2S contents.

Near the end of the life-test the systems will be operated to demonstrate NO_x reduction.

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Table 1

COMPARISON OF DESIGN AND ACTUAL PERFORMANCE DATA

	Design	Actual
SO_2 Removal Efficiency, %	90	90
Hydrogen Consumption, wt H_2/wt S	0.20	0.19
Absorber Efficiency, %	99.5	99.9
SO_2 Concentration of Stripped Water, ppm wt S	10	5
Total S Concentration of Stripped Water, ppm wt S	-	20
Influence on Claus Efficiency	None	None

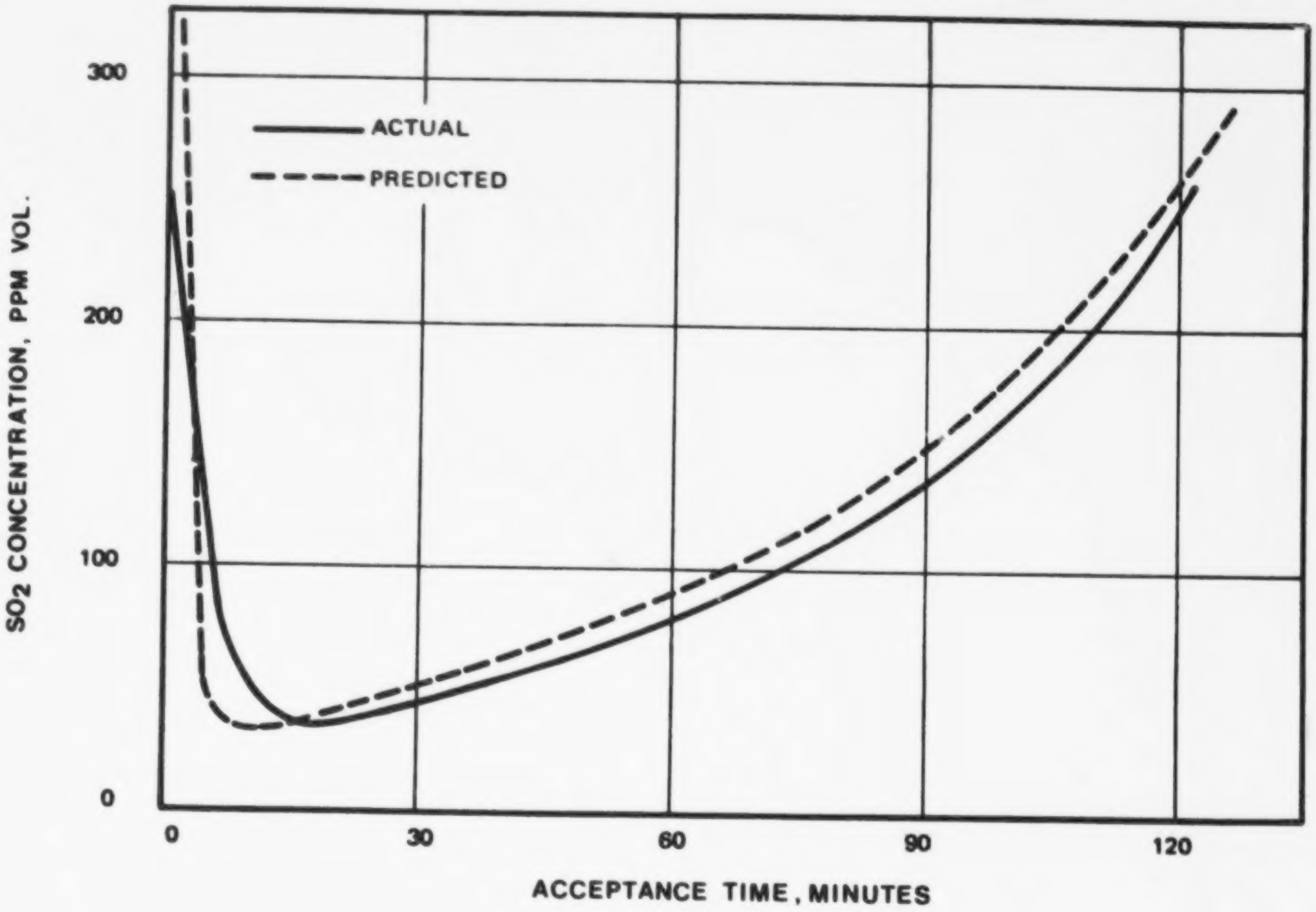


FIGURE 1

SO_2 CONCENTRATIONS IN TREATED FLUE GAS

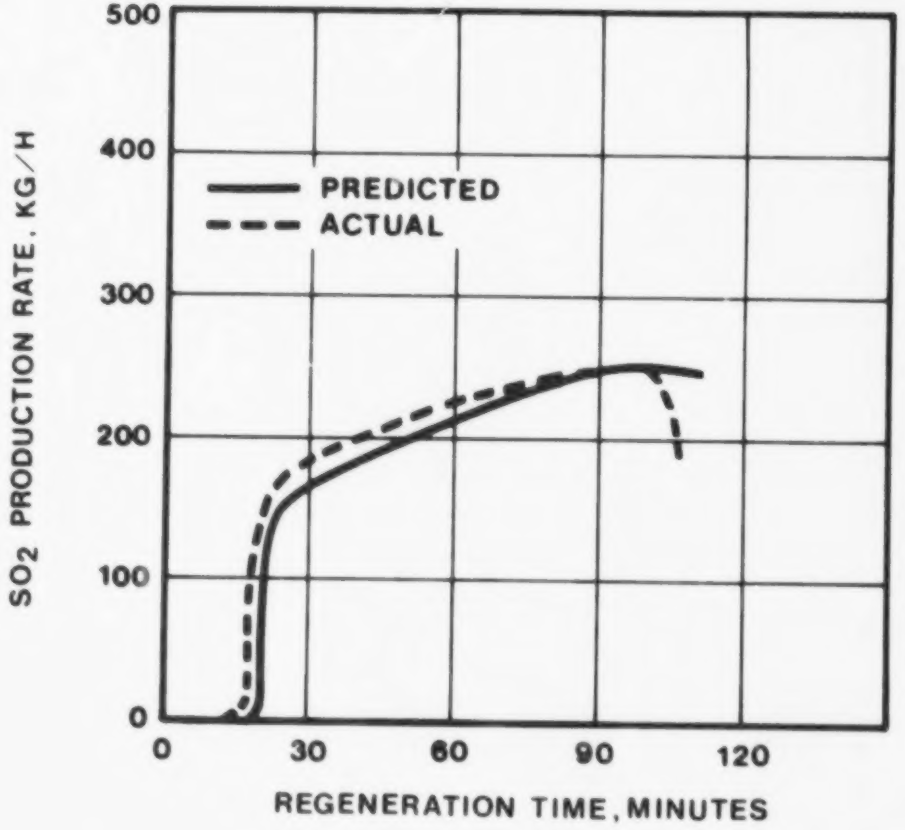
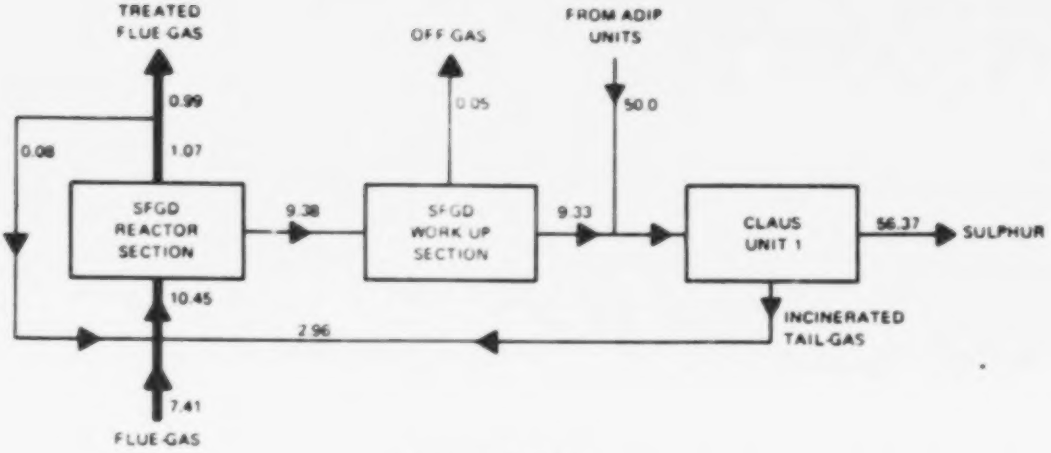
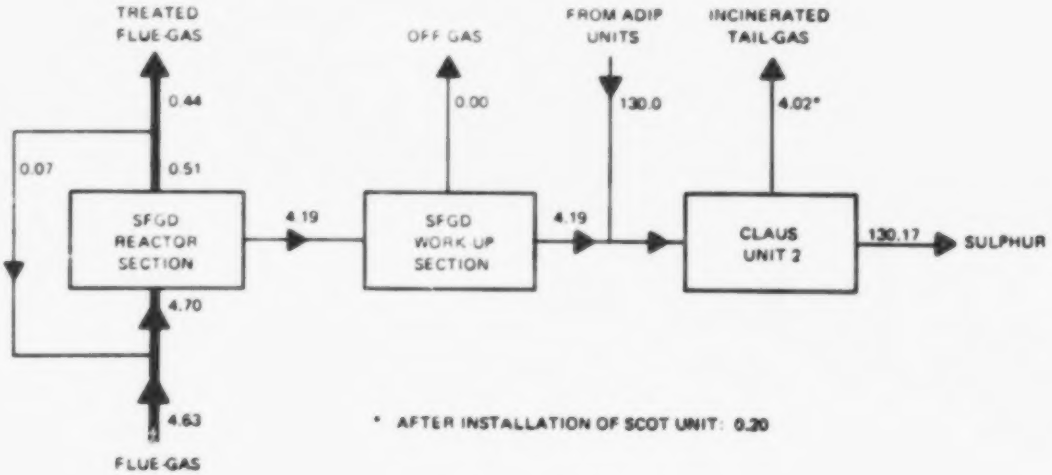


FIGURE 2

SO_2 CONCENTRATIONS IN REGENERATION OFF-GAS


TREATED FLUE-GAS
OFF GAS
FROM ADIP UNITS
0.99
0.05
50.0
0.08
1.07
SFGD REACTOR SECTION
9.38
SFGD WORK UP SECTION
9.33
CLAUS UNIT 1
56.37
SULPHUR
10.45
INCINERATED TAIL-GAS
2.96
7.41
FLUE-GAS

ORIGINAL DESIGN


TREATED FLUE-GAS
OFF GAS
FROM ADIP UNITS
INCINERATED TAIL-GAS
0.44
0.00
130.0
4.02*
0.07
0.51
SFGD REACTOR SECTION
4.19
SFGD WORK UP SECTION
4.19
CLAUS UNIT 2
130.17
SULPHUR
4.70
4.63
FLUE-GAS

* AFTER INSTALLATION OF SCOT UNIT: 0.20

ACTUAL OPERATION

FIGURE 3

SULPHUR LOADS OF SFGD UNIT AT SYS, IN TONS/DAY OF SULPHUR

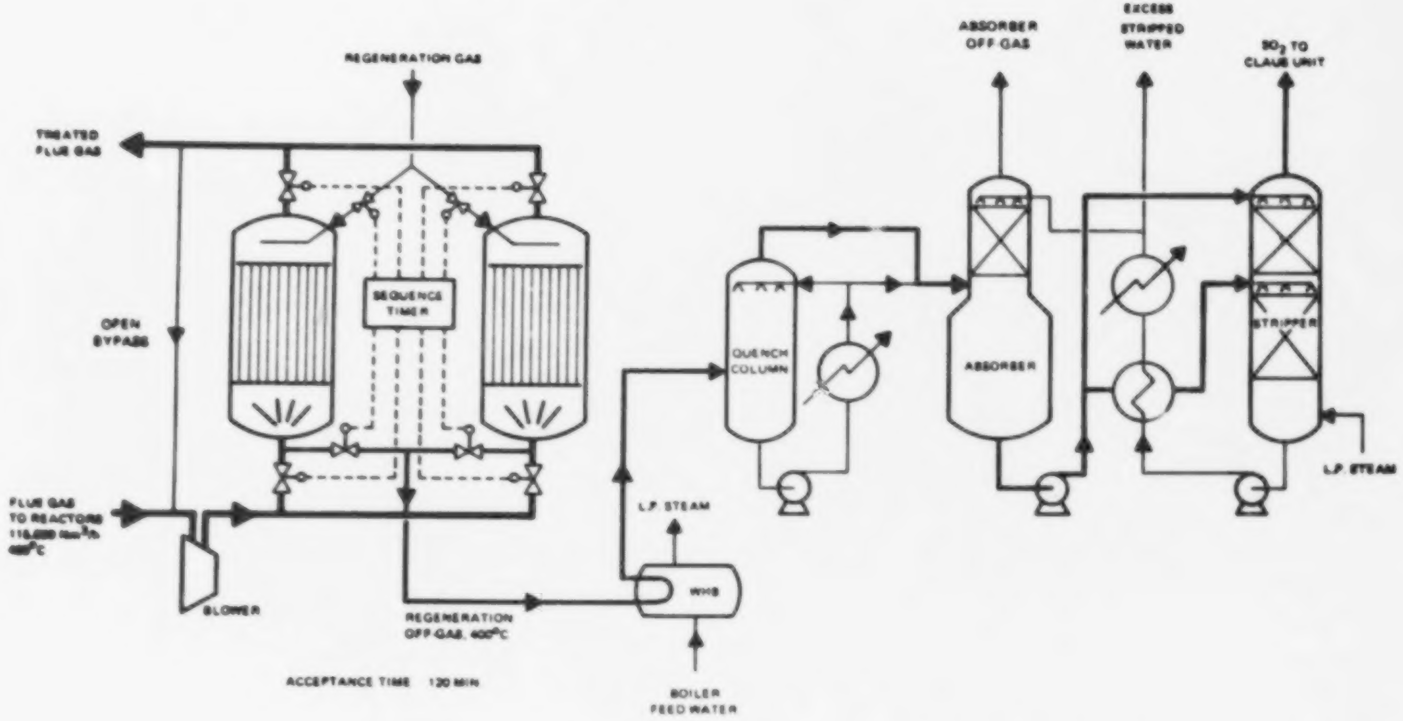

REGENERATION GAS
TREATED FLUE GAS
OPEN BYPASS
SEQUENCE TIMER
FLUE GAS TO REACTORS
BLOWER
REGENERATION OFF-GAS, 400°C
ACCEPTANCE TIME 120 MIN
L.P. STEAM
WHB
BOILER FEED WATER
QUENCH COLUMN
ABSORBER OFF-GAS
ABSORBER
EXCESS STRIPPED WATER
SO2 TO CLAUS UNIT
STRIPPER
L.P. STEAM

FIGURE 4

SIMPLIFIED PROCESS FLOW SCHEME OF SFGD UNIT AT SYS

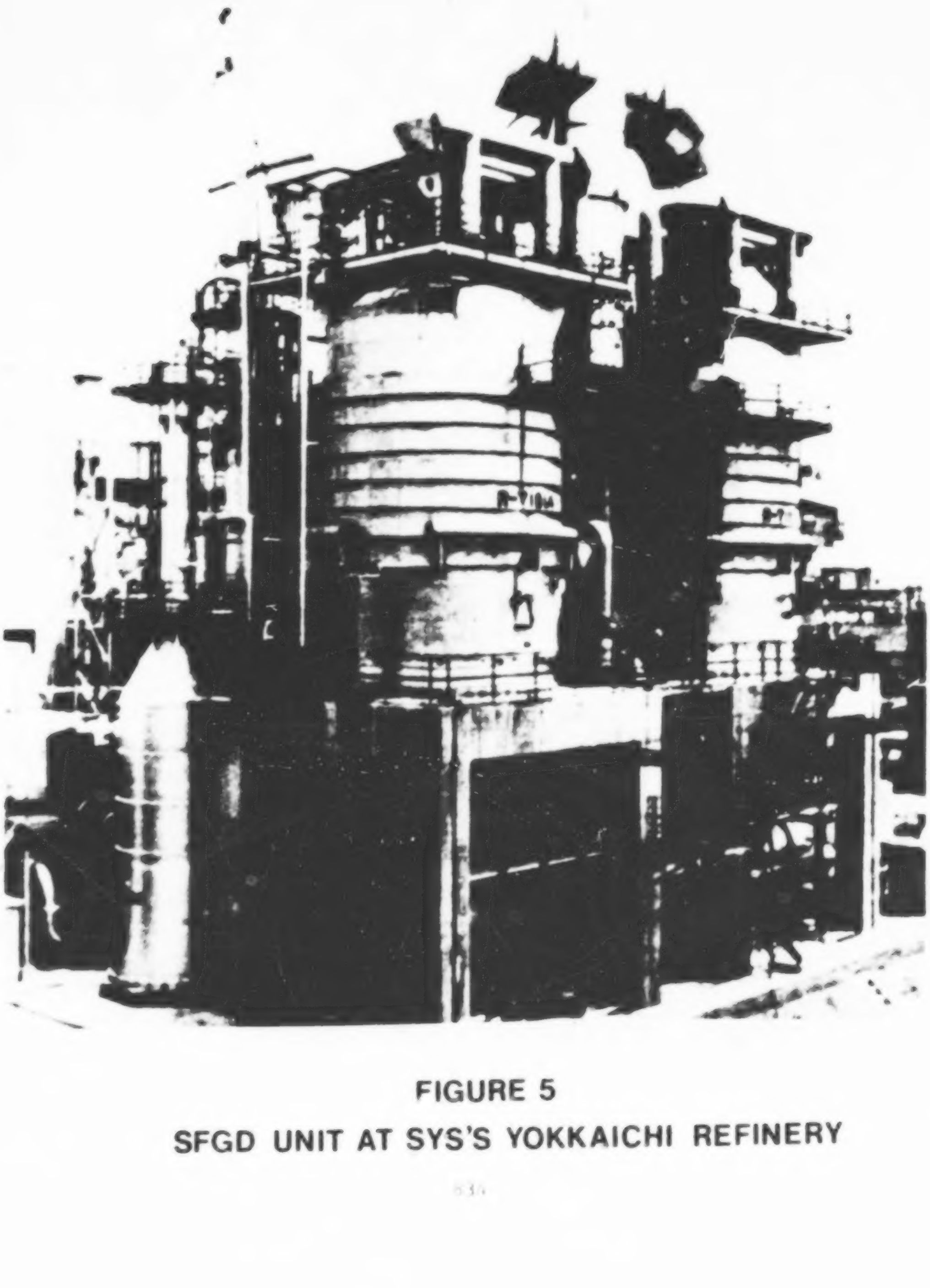


FIGURE 5
SFGD UNIT AT SYS'S YOKKAICHI REFINERY

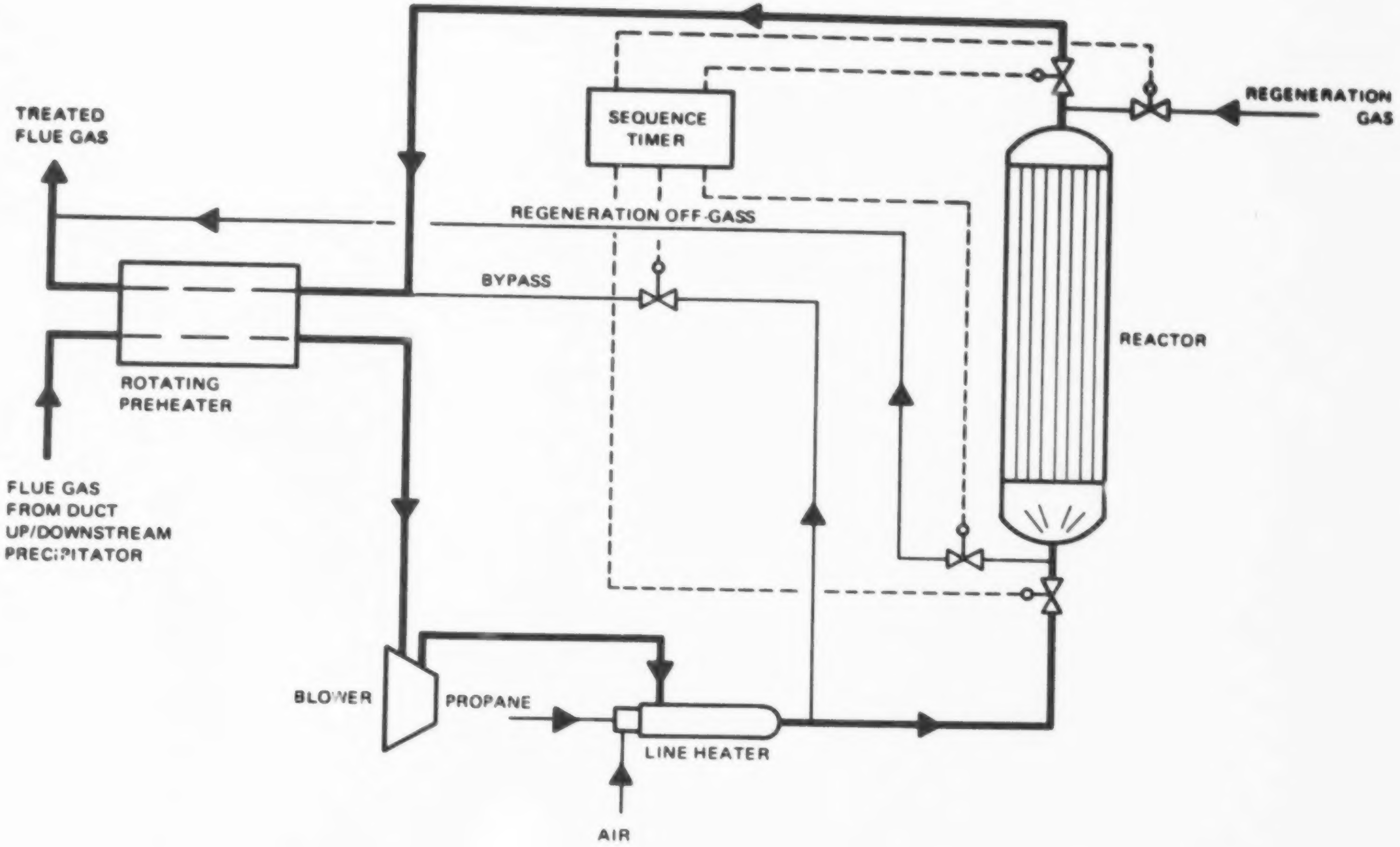

REGENERATION GAS
SEQUENCE TIMER
TREATED FLUE GAS
REGENERATION OFF-GASS
BYPASS
REACTOR
ROTATING PREHEATER
FLUE GAS FROM DUCT UP/DOWNSTREAM PRECIPITATOR
BLOWER
PROPANE
LINE HEATER
AIR

FIGURE 6
SIMPLIFIED FLOW SCHEME OF SFGD DEMONSTRATION UNIT FOR COAL FIRED UTILITY BOILER AT TAMPA ELECTRIC, FLORIDA

STATUS REPORT
ON
CHIYODA THOROUGHBRED 101 PROCESS

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ABSTRACT

This process uses water to absorb SO_2, which is oxidized by air to yield sulfuric acid. The resulting weak acid is actually circulated as an absorbent of SO_2, and a part is neutralized with limestone to produce the by-product gypsum. The gypsum is recoverable as wallboard or as a cement retarder, depending on local conditions.

Ten commercial plants have been already commissioned in Japan including a 250MW power plant application, which will be followed by several plants now under construction. After slight modification all plants are running quite satisfactorily with over 90% removal of SO_2.

All applications on boilers in Japan are treating oil burnt gas. Therefore, a demonstration plant for coal burnt gas has been constructed in Florida to likewise prove the process.

Numerous studies in a laboratory for catalyst activity with impurities from coal have been conducted. Comprehensive study is also being done to optimize and economize the plant for large applications and to improve it for better air pollution abatement processing.

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Status Report on
Chiyoda THOROUGHBRED 101 Process

1. INTRODUCTION

Several scrubbing processes in Japan and in the United States are currently reputed as highly developed for removing SO_2 from waste gases. The Chiyoda THOROUGHBRED 101 (CT-101) Process is also highly appraised in Japan with its dry, marketable by-product and simple operation. Ten plants are operating smoothly and five others are under construction in Japan and in the United States (Table 1), three years after the process was announced by Chiyoda Chemical Engineering & Construction Company. The largest plant now operating is for Hokuriku Electric Power Company at its 250MW boiler in Toyama, and a 350MW plant is now under construction for the same utility company. All CT-101 applications for boilers in Japan are treating oil-fired gases, because of lack of coal resources there. Recently Chiyoda International Corporation (CIC) was established in Seattle, Washington to introduce the process to the United States. CIC is constructing a demonstration plant at Scholz Plant of Gulf Power Company in Sneads, Florida for coal-fired application.

The purpose of this paper will cover the CT-101 process, plants and operations.

2. PROCESS DESCRIPTION

A simplified flow diagram is given in Figure 1. Flue gas generated in a boiler or an incinerator, is introduced into a venturi type prescrubber to remove particulates and to be cooled down. For gases, heavily loaded with particulates, as from coal-burning power plant boilers, it is desirable to have an electrostatic precipitator before the Chiyoda system to remove most of the particulates.

The flue gas is then fed into the absorber where SO_2 is absorbed by water. The absorption is countercurrent, that is, the gas enters at the bottom and the absorbent at the top. The absorber is a tower with packing supported on grids. The gas leaving the absorber is reheated to restore buoyancy and to reduce the incidence of a visible steam plume.

The scrubber effluent solution flows to the oxidizer tower where air bubbled through the liquor converts all the absorbed SO_2 to H_2SO_4, with the help of ferric ion dissolved as a catalyst. Part of the liquor leaving the oxidizer passes to gypsum production and the remainder is recycled to the absorber. Thus, the recycling absorbent is dilute sulfuric acid solution with a concentration of about 2 to 5%. In the absorber, oxygen in the recycling liquor and in the flue gas oxidize the absorbed SO_2, thus improving the abosrption capacity of the liquor.

The sidestream from the oxidizer is neutralized with lime or limestone to crystallize gypsum. Chiyoda has developed a crystallizer capable of producing crystals suitable to be dehydrated by conventional centrifuges. The mother liquor leaving the crystal is recycled to the adsorber. Final chemistry is as follows:

$$
\begin{aligned}
SO_2 &+ H_2O \longrightarrow H_2SO_3 \\
H_2SO_3 &+ 1/2\ O_2 \longrightarrow H_2SO_4 \\
H_2SO_4 &+ CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2
\end{aligned}
$$

3. FEATURES

3-1. Simple Process Flow

The CT-101 process has quite a simple plant structure. That is,

1) The process itself is simple, using few vessels.
2) The plant is composed of simple, already known but valuable apparatus of each unit operation, except the gypsum crystallizer.
3) No slurry is used in the absorber where flue gas passes through, securring no clogging problems.

Therefore, the process promises easy operation, wide range of operational flexibility and stable operation.

3-2. High Efficiency Desulfurization

SO_2 in the cleaned gas can be held to 50ppm or lower. In other words, more than 95% desulfurization is easily attainable, because of the combination of the absorber and the oxidizer and the usage of Fe^{+++} catalyst.

3-3. Dry By-product Gypsum

Gypsum is a highly stable chemical compound of sulfur, that is harmless when stored. The by-product of CT-101 contains only about 10% of free water, therefore, it can be readily stock-piled without the slump problems which normally occur when excessive moisture is present. Transportation is a simple matter which can be accomplished by utilizing dump trucks. Furthermore, the by-product gypsum, can be recoverable as a wallboard and cement constituent as has been done in Japan.

4. HISTORY OF DEVELOPMENT

Investigation and analysis of referential literature covering all proposed processes for stack gas cleaning, including dry and wet processes was performed and a suggestion for the process written by Johnstone in 1931 (Reference 1) was found promising. Starting by tracing the original paper, the process was developed in the following manner:

4-1. Laboratory Work

A series of experiments was conducted to locate a possible catalyst. Earlier attempts by Copson et al (Reference 2, 3) were focused primarily on manganous sulfate as catalyst because of its high activity, but not industrialized of poisoned catalyst by contaminants carried in the gas and others. Ferric ion was chosen because of its harmlessness, availability and stability to the possible contaminants as on Table 2, Fe^{+++}

is active enough comparing with Mn^{++} catalyst, as shown on Figure 2, at the temperature that usual flue gases reach when directly contacted by water.

4-2. Bench Test (December 1970 - June 1971)

Bench scale tests were conducted using flue gas of 50 Nm^3/hr generated by burning fuel oil. During this period the main effort was concentrated on collecting absorption and oxidation process data. SO_2 and other components were added to the gas when needed.

4-3. Pilot Test (July 1971 -)

A pilot plant with a capacity of 1000 Nm^3/hr was constructed to collect data necessary to design equipment for commercial application, including gypsum production. Bunker oil, sometimes mixed with asphalt was burned in the incinerator. After three months operation proved the reliability of the process, the process was introduced to Japanese industry in October 1971. Laboratory work is still being continued to collect catalyst stability data and to analyze reaction mechanism.

5. PRIMARY COMMERCIAL PLANTS

After the introduction of CT-101, four plants were designed and constructed almost simultaneously. These plants encountered several problems. However they have already been overcome as follows and all plants are now running quite satisfactorily.

1) Too slow flowing velocity in horizontal pipings caused gypsum deposits. Pipings were inclined and smaller sized pipes were adopted.

2) Gypsum erroded rubber lined glove valves which were changed to stainless steel valves of a different style.

3) Air spargers for oxidation were plugged by gypsum crystals. To eliminate this trouble, a clarifier was installed to minimize carry-over of gypsum crystals in recycling absorbent from the centrifuge. Sparger holes were enlarges and air was cooled down before entering the oxidizer.

4) By-product gypsum contained more than 15% of free water that would decrease dryer capacity of wallboard manufacturer and become difficult of bulk handling with dump trucks. The crystallizers were redesigned with longer holding time of crystals to obtain a larger crystal size for easier dewatering in the centrifuge.

5) Pitting corrosions on some parts of stainless steel plates caused by the accumulated chlorine ions in the absorbent when burning low grade oil. The limitation of chlorine content was reduced to 200ppm by adjusting a purge rate.

6. LARGE SCALE PLANTS

Several large scale plants have been under construction, and two of them were commissioned in June of this year, one for Hokuriku Electric Power Co. and the other for Mitsubishi Chemical Co.

6-1. Plant Outline

For Hokuriku the design was started in November 1972 and concrete was poured July 1973 for foundation work. Hot gas was introduced on June 4th of this year. With the exception of one month intermission in July for inspection of both boiler and turbine which were constructed at the same time, the plant has been running very satisfactorily.

A general layout of this desulfurization unit is given in Figure 3. The whole SO_2 removal process is located in 5,000 m^2. The crystallization process is done in a separate area from the absorption section leaving an area for future expansion.

The main feature of the Hokuriku plant is in the absorption and the oxidation apparatus. They are combined in one cylindrical column. That is, the column consists of two concentrical shells with a center area for the oxidation and an annuli for the absorption. This configuration is good for the internal supports in mechanical strength and also helpful for liquid distribution at the top of the column. Table 3, shows the specification of the main apparatus. Stainless steel, FRP, rubber lining, etc. can be applied for construction materials without difficulties. Chiyoda International Corporation estimates roughly the CT-101 plant cost in the U. S. will be in the range of $80 - 100/kw for a 250MW power plant.

6-2. Operation

Operational data obtained in both plants are described in Table 4. The Hokuriku Plant is extracting half of the flue gas from a 500MW boiler. Instrumentation allows gas fluctuation according to boiler operation in the range of 25 to 100% of gas treating capacity. The plant is treating gas by burning 1% sulfur oil, however, it can treat gas of 3% sulfur oil in the future when the facility will be doubled to treat all the gas generated in the boiler.

The plant is operated by two people per shift; except when solids are handled such as, unloading limestone and loading gypsum into trucks. Almost all plant apparatus can be operated and their performances can be observed at the control panel room. The plant performances demonstrates that the process serves for pollution abatement, that is, for removal of SO_2 and fine particulates. The SO_2 level is reduced to below 30ppm at the stack outlet. Particulates, are also removed to 16.5 mg/Nm^3 from 280 mg/Nm^3.

Gypsum is being sold to wallboard manufacturers and cement companies at good prices. Bleed stream from the system to maintain the concentration of cholrine and others is disposed after recovery of catalyst dissolved, being controlled of pH and removed of suspended solids. The final properties of water meet the waste water qualification regulation.

Generally the properties are as follows:

pH	6.5 -- 7.5
COD	less than 15ppm
Suspended Solid	less than 30ppm

7. APPLICATION FOR COAL-BURNING

CT-101 units are being applied successfully for oil-burnt flue gas in Japan. However, there is no application for coal gas. The main difference between oil and coal-burnt gases would be in particulates loading and compositions of fly ash and gas.

Grain removal is recommended by installing some device before the process, such as an electrostatic precipitator to reduce it to be below 2000 mg/Nm^3. After using such a dust collector in the process, particulates will be removed by prescrubbing first and next by simultaneous SO_2 absorption.

Several kinds of fly ash collected in the U. S. utility boilers were added in the absorbent of test units in Kawasaki Laboratory of Chiyoda and the results obtained indicates CT-101 application of coal gas without trouble. Also, individual components of the fly ash and organic constituents in the coal gas were investigated in the same manner. Some results are tabulated in Table 2.

Meanwhile, Gulf Power Co. has a testing project for SO_2 removal using several kinds of U. S. coal. The decision was made to join the project and to demonstrate the process in the U. S. The plant has a capacity equivalent to 23MW. The gas flow rate will follow the fluctuation of the boiler operation. Before the process, an electrostatic precipitator has been installed of which particulate removal efficiency will be adjusted accordingly with test schedules to obtain data on a wide range grain loading into the stack gas cleaning process. The plant will be completed within this year.

8. FUTURE

We anticipate successful operation of CT-101 process at the Florida plant which will demonstrate process applicability to coal burning boilers. Besides, studies are being continued for better construction materials, processing apparatus, economics and for a better abatement process. One of such achievements is the process for simultaneous removal of SO_2 and NO_x, basically using the CT-101 process with addition of an O_3 generator. (Reference 4)

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TABLES

1. LIST OF COMMERCIAL PLANTS
2. PARTIAL LIST OF CHEMICALS TESTED IN LAB FOR CATALYST ACTIVITY
3. EQUIPMENT LIST
4. TYPICAL OPERATIONAL DATA

Figures

1. Process flow diagram
2. Catalyst activity
3. General layout of Hokuriku Electric Co., plant

Table 1, LIST OF COMMERCIAL PLANTS

Owner of plant	Location	Nm^3/hr	Gas source	Completion
1. Nippon Minning Co.	Mizushima	33,500	Claus	Nov. 1972
2. Fuji Kosan Co.	Kainan	157,200	Boiler & Claus	Nov. 1972
3. Mitsubishi Rayon Co.	Otake	90,000	Boiler	Jan. 1973
4. Tohoku Oil Co.	Sendai	14,000	Claus	Feb. 1973
5. Daicel Co.	Aboshi	100,000	Boiler	Nov. 1973
6. Amagasaki Coke Co.	Kakogawa	36,200	Gas incinerator	Feb. 1974
7. Hokuriku Elect. Co.	Toyama	750,000	Power boiler (250MW)	June 1974
8. Mitsubishi Chem. Co.	Yokkaichi	400,000	Boiler	June 1974
9. Mitsubishi Pet. Chem. Co.	Yokkaichi	150,000	Boiler	Sept. 1974
10. Mitsubishi Pet. Chem. Co.	Yokkaichi	700,000	Boiler	Oct. 1974
11. Gulf Power Co.	Florida	90,000	Power boiler (23MW)	Nov. 1974
12. Denki Kagaku Co.	Chiba	120,000	Boiler	Feb. 1975
13. Hokuriku Elect. Co.	Fukui	1,050,000	Power boiler (350MW)	May 1975
14. --- Elect. Co.	---	750,000	Power boiler (250MW)	Oct. 1975
15. --- Elect. Co.	---	750,000	Power boiler (250MW)	Spring 1976

Table 2, PARTIAL LIST OF CHEMICALS TESTED IN LAB FOR CATALYST STABILITY

1. All chemicals listed do not have negative influence on catalyst activity in CT-101 process.

2. Test Condition

Catalyst	Fe^{+++}	2000ppm
Absorbent	Free H_2SO_4	2.2wt%

3. Concentration in numerals gives only the maximum valve tested and not the limitation.

Component	ppm	Component	ppm as ion
Formaldehyde	300	V_2O_5	100
Acetaldehyde	800	V_2O_5	500
		+NiO	100
m-Tolualdehyde	100	$NiSO_4$	1,000
Phenol	100	Metal Cr	500
Resorcinol	100	$PbO+PbSO_4$	5
Phlorogrucinol	300	H_3ASO_4	10
Acetaldehyde	300	Metal Sn	100
+ Resorcinol	100		
		Na_2SO_4	10,000
Acetaldehyde	800	$MgSO_4$	10,000
+ Phenol	200		
Fluoranthene	30	$(NH_4)_2SO_4$	15% as $(NH_4)_2SO_4$
+ Perylene	30		
+ Benzopyrene	30	HCl	200
+ Pyrene	30		
Ditto	ditto	HNO_3	1,000
+ Ether	+1%		

Table 3, EQUIPMENT LIST
Hokuriku Electric Power Company
250MW CT-101 Unit

No.	Name	Type	Dimensions	Quantity
1.	Precooler	Venturi	----	2
2.	Abs-Oxidizer	Double shells	Diameter 21m Height 28m	1
3.	Absorbent Tank	Cone roof	5,000 m^3	1
4.	Limestone Silo	with bag filter	500 m^3	1
5.	Limestone Slurry Tank	Agitated	40 m^3	1
6.	Crystallizer	Agitated	500 m^3	1
7.	Clarifier	with rake	300 m^3	1
8.	Centrifuge	Basket	----	3
9.	Flue Gas Fan	Turbo	750,000 Nm^3/hr	1
10.	Air Blower	Turbo	7,500 Nm^3/hr	2
11.	Absorbent Pump	Double suction	----	3
12.	Mist Eliminator	Chevron	----	1

Table 4, TYPICAL OPERATION DATA

Owner of plant		Hokuriku Electric Power Co.	Mitsubishi Chemical Co.
Gas source		Oil burnt boiler	Oil burnt boiler
Operational data			
Flue gas rate	m^3/hr	750,000	324,000*
Boiler capacity equiv.	MW	250	110
SO_2 In	ppm	436	780
Out	ppm	21	25
Removal	%	94 7	97.3
H_2SO_4 in Absorbent	%	2.2	1.8
Limestone	ton/day	34.8	27.1
Elect. power	KW	4,500	3,400
Water	ton/hr	45	20

* Boiler is loaded to 80% of capacity in summer.

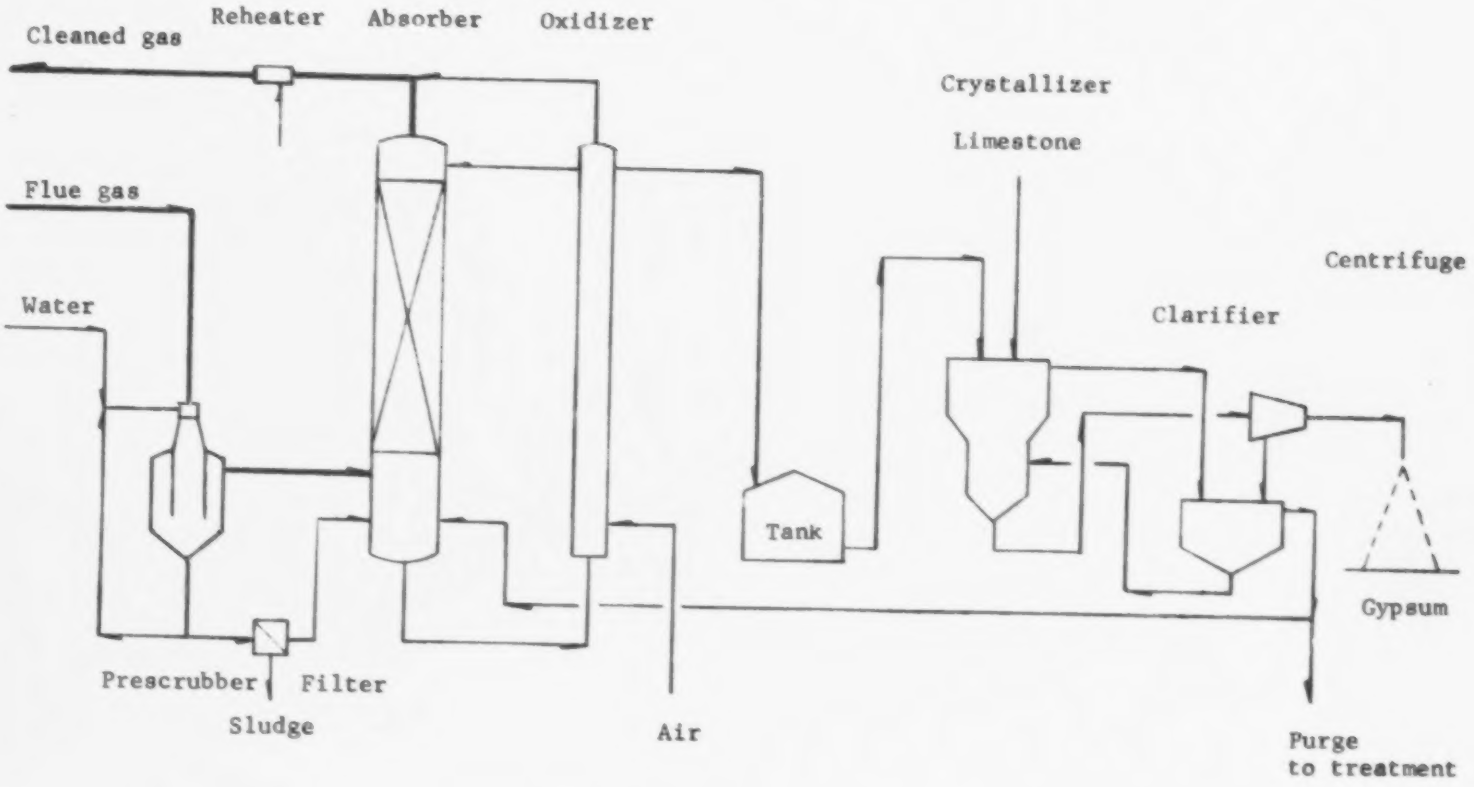

Cleaned gas
Reheater
Absorber
Oxidizer
Crystallizer
Limestone
Flue gas
Centrifuge
Water
Clarifier
Tank
Gypsum
Prescrubber
Filter
Sludge
Air
Purge
to treatment

Figure 1, Process flow diagram

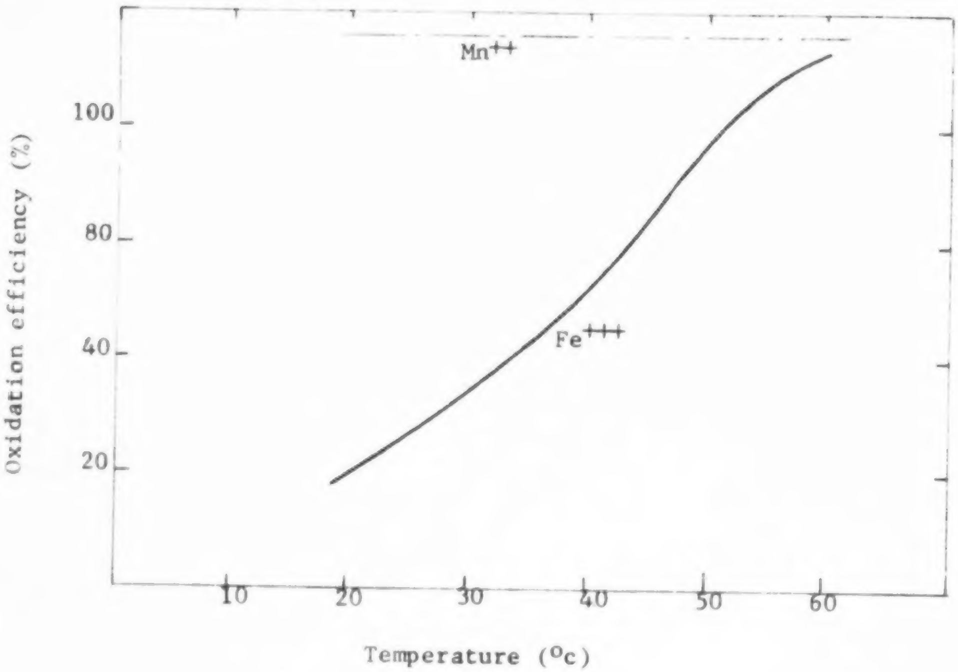
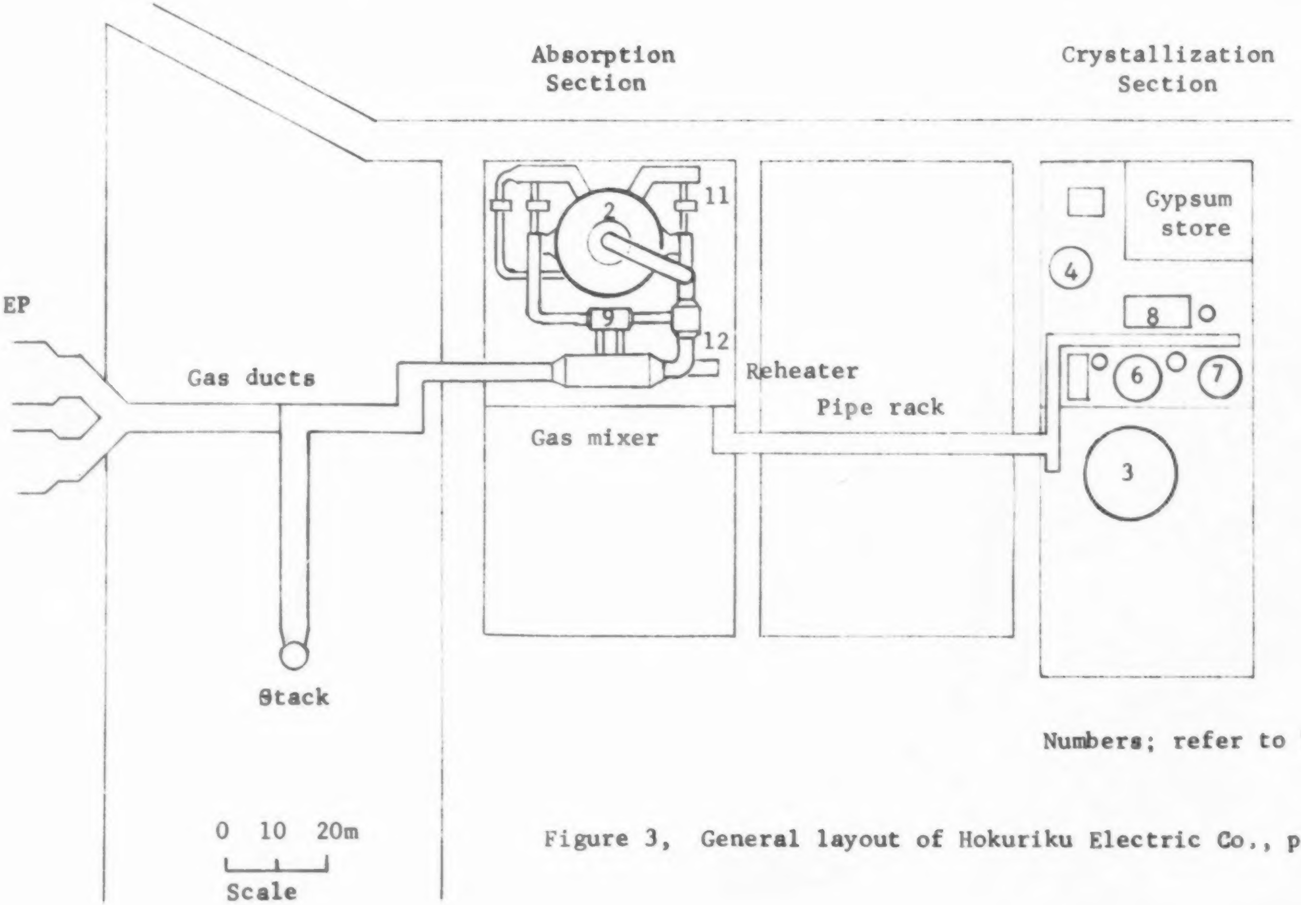


Figure 2, Catalyst activity


Absorption Section
Crystallization Section
EP
Gas ducts
2
11
9
12
Reheater
Pipe rack
Gas mixer
Gypsum store
4
8
6
7
3
Stack
0 10 20m
Scale

Numbers; refer to Table 3

Figure 3, General layout of Hokuriku Electric Co., plant

FLUE GAS DESULFURIZATION BYPRODUCT DISPOSAL/UTILIZATION

REVIEW AND STATUS

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Prepared for Presentation at
Flue Gas Desulfurization Symposium
Sponsored by the Environmental Protection Agency
Atlanta, Georgia
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FLUE GAS DESULFURIZATION BYPRODUCT DISPOSAL/UTILIZATION

REVIEW AND STATUS

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In the symposium last year, several excellent papers introduced the subject of this session and the general considerations will not be covered in this paper. For those who did not attend the last meeting in New Orleans, I recommend that a copy of the proceedings be obtained. The topics that we will cover in this discussion focus on progress in understanding and solving problems associated with disposal and use of byproducts from flue gas desulfurization processes.

During the initial period, the discussion will center on disposal of waste materials and later in the program, use of recovered products will be considered. The first paper will review the status of waste disposal from full-scale lime-limestone scrubbing systems currently installed. Then the EPA program to develop better alternatives will be reviewed, followed by a discussion of the experience with one of the methods for chemical fixation. One of the highlights of the session will be a review of the status in Japan where the emphasis is on utilization of recovered products even from lime-limestone systems. During the portion of the program directed toward work in this country on utilization, the preliminary results of market evaluations for sulfuric acid, sulfur, and gypsum will be presented. The experience with production and marketing of acid from the Boston Edison magnesium oxide scrubbing system will conclude the formal presentations after which a discussion with the audience and among the panelists is scheduled. My presentation will attempt to identify the important considerations from the utility viewpoint.

Removal of sulfur oxides from stack gas has received far more attention than the question of what to do with it after it is caught. The technology for removing SO_2 is gradually evolving to the point that within a year or two, alternative methods probably will be available for use where they are needed. A very real concern in considering use of the technology is disposal of products. Recurring questions include:

- How much is produced?
- What are the choices?
- For throwaway processes, how do I throw it and where is away?

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- For recovery processes, is the market reliable for continuous production of varying amounts and what happens if the pipeline clogs?
- Are the rules going to change?
- What is the cheapest way out?

Of course, no one has all the answers at present but reliable responses are needed to provide the guidance required for intelligent process selection. The following discussion will help to give perspective to some of the concerns.

HOW MUCH IS PRODUCED?

The quantity produced for a single installation depends on several factors including process used, the sulfur content of the fuel, the extent of control required, and the load factor for the plant; the quantity on a national basis depends on how many sources will use desulfurization systems. There probably is no such thing as a typical installation, but for example, a 500-MW power plant with an average load factor of 60% and burning 3.5% S coal would produce about one-half million tons (dry basis) of waste over a 25-year period when equipped with a limestone scrubbing system to meet the new source performance standard; the volume of solids (50% moisture) produced would occupy approximately 6000 acre-feet. Installation of a recovery process to produce sulfuric acid at the same plant would result in about 85,000 tons per year of acid.

The number of plants that will be equipped with stack gas cleaning systems is uncertain. In spite of a general preference for use of low-sulfur fuels to meet emission requirements, several utilities are proceeding with plans for installation of desulfurization systems either because of insufficient supplies of low-sulfur fuel or because of potential economic advantages.

One trend is apparent--nuclear generation capacity has not reached the level of earlier forecasts (Figure 1)[1,2] and with the emphasis for use of gas and oil elsewhere, coal is likely to be the primary fuel for power generation for many years to come. On the other hand, energy conservation measures may decrease the growth rate for power demand. This has been partially responsible for deferment of some new power plant construction in recent months.

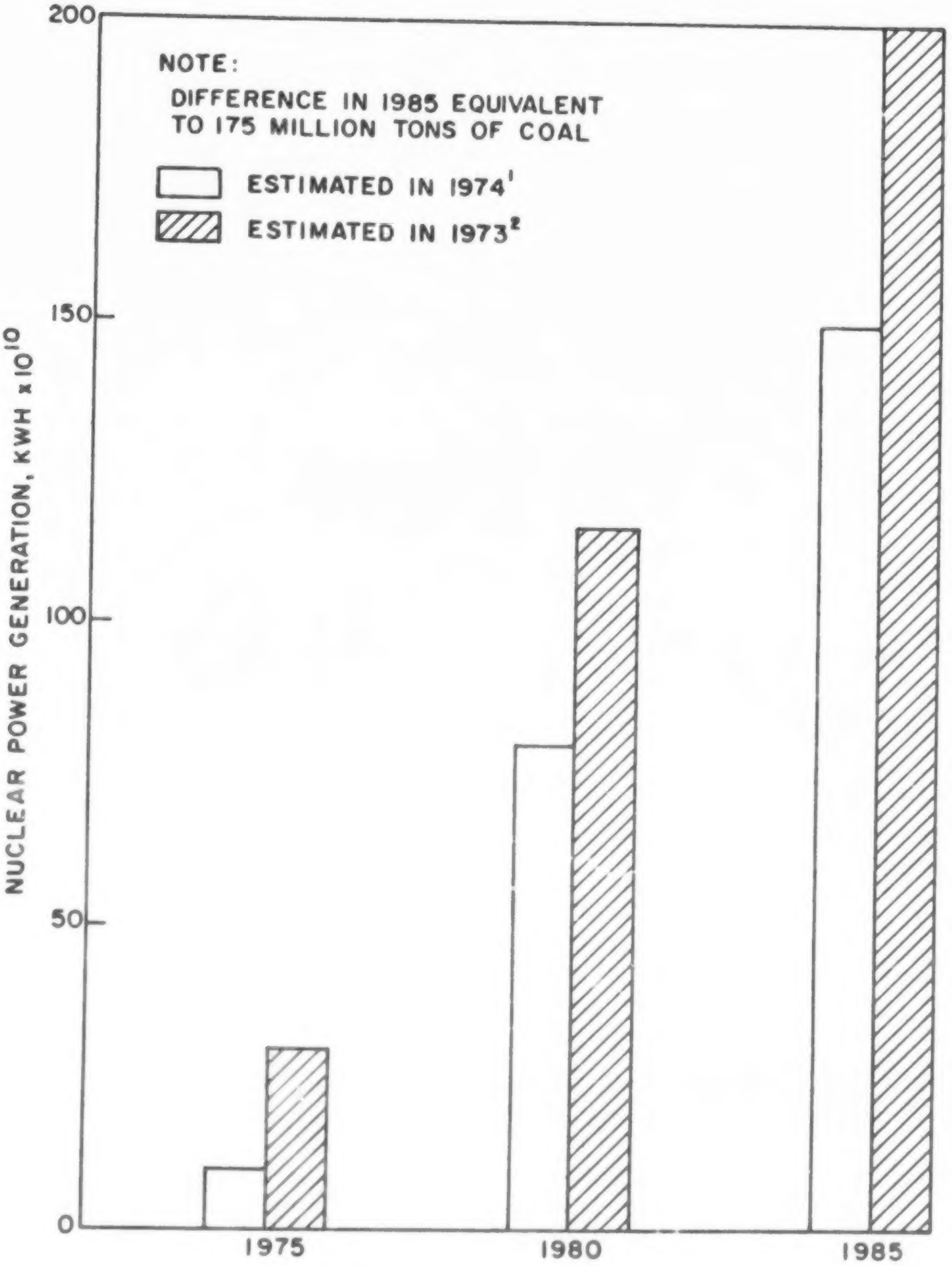

Figure 1. Projected Nuclear Power Generation

Future energy requirements were estimated in a recent report prepared for the Office of Coal Research, U.S. Department of Interior, by the Hudson Institute.[1] The coal needed to meet the direct combustion energy demands through 1985 is shown in Figure 2. To develop the capability to produce and deliver the estimated amounts will require heroic effort. About 76% of the states have SO_2 regulations that limit sulfur content of coal to 1% or less, but in 1970 only 13% of the coal used by utilities had less than 1% sulfur.[1] Incentives to produce low-sulfur coal will probably improve the ratio of low to high-sulfur coal and an arbitrary assumption of 30% low S in 1985 will allow some estimates of desulfurization product quantities. Further assumptions are average sulfur content of 4% (high sulfur fraction only), 80% removal, and 50% of the high-sulfur coal is used in installations equipped with flue gas desulfurization systems. On this basis, the total sulfur removed would be 20 million tons annually.

Recovery of this amount in calcium-based wet scrubbing systems would require approximately 200,000 acre-feet per year of storage for waste disposal. Conversion to sulfuric acid would result in production of 60 million annual tons of acid, an amount that exceeds the total projected market. No one suggests that a single method will be used universally. Instead, a variety of processes will probably result in a mix of throwaway and recovery products.

WHAT ARE THE CHOICES?

Several different processes are being tested in full-scale facilities and others are planned. Depending on successful completion of continuing development work, the list of candidate processes for sulfur oxide control could include the methods listed below.

Processes that Produce Waste Products

- Limestone scrubbing
- Lime scrubbing
- Double alkali (sodium or ammonia with lime or limestone)
- Dilute acid neutralization with lime or limestone
- Sodium salt scrubbing

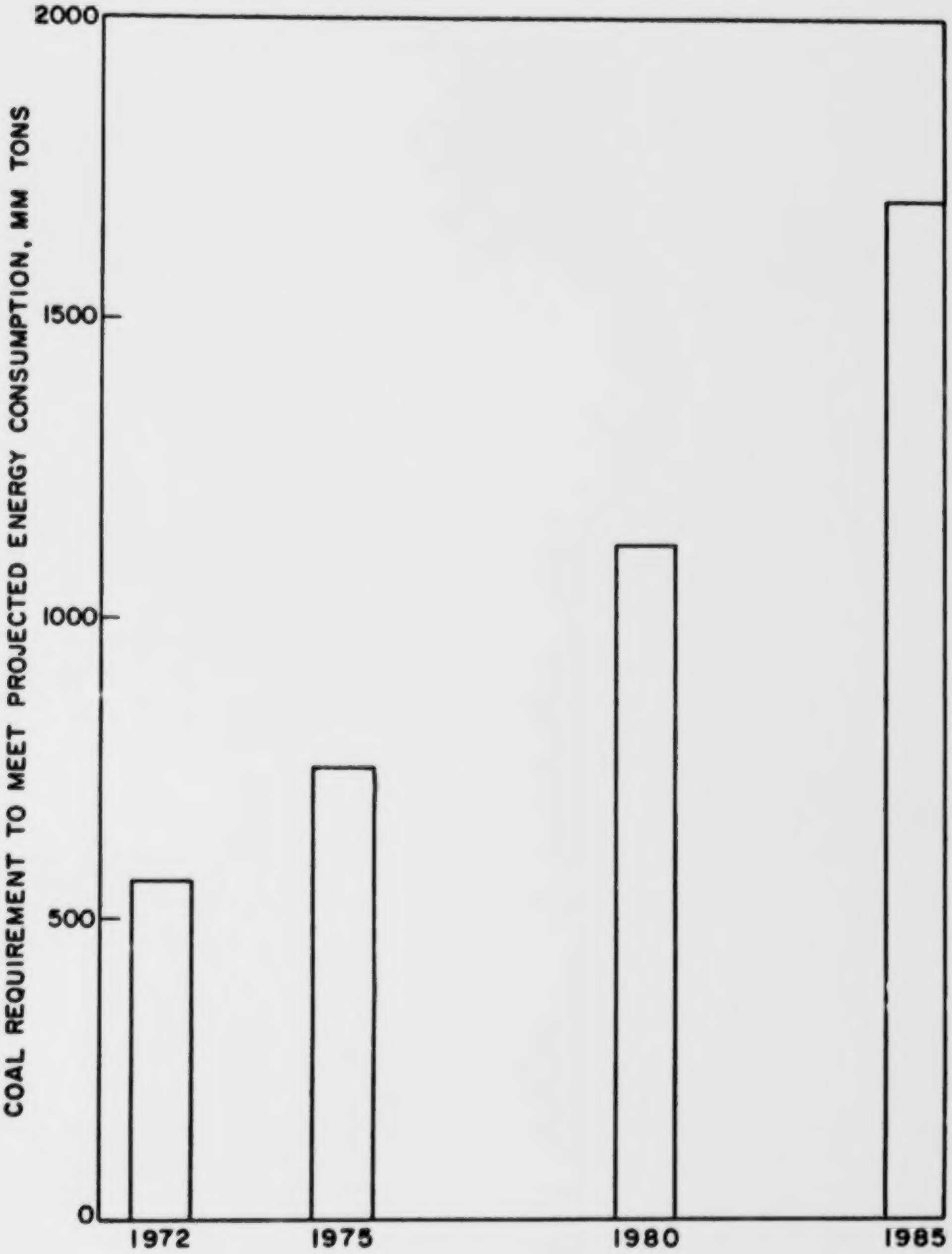

Figure 2. Estimated Future Coal Requirements[1]

Limestone and lime scrubbing systems account for most of the large-scale installations primarily because development work has been focused on these methods. Use of limestone generally produces more waste solids than use of lime because a larger amount of excess absorbent is required for comparable removal. The sludge storage characteristics are poor except when oxidation of sulfite to sulfate is essentially complete. High oxidation can sometimes be achieved directly in the scrubber when the SO_2 concentration in the gas is low. A separate oxidation step is used in some processes. Interest in the double alkali method stems from operating problems with slurry scrubbing. The problems can be avoided by scrubbing with a soluble salt and precipitating the absorbed sulfur oxide as a waste material by addition of lime or limestone; the properties of the waste solids are similar to those produced directly in the scrubber. Dilute acid neutralization with lime or limestone has the advantage of producing an essentially completely oxidized product. Dilute acid may be produced by absorption of SO_2 in a solution containing an oxidation catalyst or by carbon adsorption and subsequent washing. Sodium salt scrubbing to produce a waste product is uniquely suited to applications where abundant natural sodium carbonate deposits are available and where solar evaporation can be used to dewater the waste stream.

Although calcium reaction products are normally considered waste materials, gypsum (calcium sulfate) has potential for use as a material for wallboard construction or for use as a cement additive. TVA has carried out a preliminary study[3] for EPA on the market for by-product gypsum in the wallboard industry.

Processes that Recover Sulfur in a Useful Form

Magnesium oxide scrubbing with thermal regeneration

Sodium salt scrubbing with thermal regeneration

Catalytic oxidation

Copper oxide - dry absorption-reduction

Except for the catalytic oxidation process, these recovery methods produce an intermediate, relatively concentrated stream of sulfur dioxide that can be converted in conventional equipment into sulfuric acid or can be reduced to elemental sulfur. Catalytic oxidation converts the dilute sulfur dioxide in the total gas to SO_3 and produces sulfuric acid directly. The yield of products (sulfur equivalent) is similar for all of the methods. The magnesium oxide method requires scrubbing with a slurry and involves solids handling for regeneration and recycle. Sodium salt scrubbing permits use of a solution in the scrubber, but heat requirements for regeneration are relatively high and oxidation complicates the process. Catalytic oxidation requires good particulate removal ahead of the process, operates at a high temperature (800°F), and produces acid that is less concentrated than standard grades. Like the catalytic oxidation method, the copper oxide dry absorption method requires no reheat of the exit gas, but since the absorption beds are fixed, gas switching is necessary.

The most logical recovery product is sulfuric acid because most of the sulfur used is in this form. However, tank storage is required to allow for distribution upsets. The most practical form for storage and shipping is elemental sulfur, but the technology to reduce SO_2 complicates the processes and most of it would have to be reoxidized for eventual use. Moreover, natural gas is the conventional source of reductant and the limited supply could affect both the availability and economics. Technology is needed to use coal as the source of reducing gas or solid for the conversion to sulfur; development work is in progress.

In addition to the basic sulfur products, acid and elemental sulfur, processes that produce fertilizers and intermediates for the pulp and paper industry are also being studied. These markets will be limited, but they may add to the alternatives for specialized market situations.

FOR THROWAWAY PROCESSES--HOW DO I THROW IT AND WHERE IS AWAY?

It is almost certain that discharge of significant quantities of waste solids to inland streams will not be acceptable.

An important question that has not been adequately answered is the extent of clarified liquor discharge or seepage that will be acceptable from the standpoint of water quality. The simplest method for disposal of the waste solids and the best approach for enhancing scrubbing system reliability is to discharge a side stream from the scrubber loop to a settling pond and to overflow the clarified liquor to a receiving stream. Because of the low solubility of calcium sulfite and sulfate, the total dissolved solids concentration is low. The volume can be reduced by use of a thickener to concentrate the solids in the stream from the scrubber. This technique is being used in some of the installations. However, the objective for development work on lime-limestone scrubbing systems has been to operate with no liquor discharge.

For closed-loop operation, pond management becomes a problem. The goal is to minimize seepage and to return the total outflow to the scrubber system. Is the local soil sufficiently impermeable so that a liner is not required? Does the pond system need to have sufficient storage volume to accommodate short-term precipitation? How is the water balance maintained where long-term precipitation exceeds evaporation? The answers to these questions may vary for each specific installation, but some guidelines are needed. The pond management problem can be avoided by mechanical dewatering of the scrubber solids so that all of the recoverable liquor is retained in the system. However, filtered or centrifuged sludge generally contains about 50% moisture and is structurally unstable; it is not suitable for landfill. Compaction may be a feasible means for improving the stability, but the solids revert to the characteristic sludge properties when exposed to water. Also, soluble components may be leached out.

The most sophisticated (and expensive) technology being developed for disposal of waste solids involves chemical fixation to improve both the physical properties and the resistance to leaching. Several companies now offer processes based on this approach and the technology is being tested on operating systems. Chemical fixation is apparently somewhat empirical and depends on sludge composition; the composition is a variable not only among different applications of lime or limestone scrubbing, but also in any specific system where ash content, excess absorbent, oxidation, and moisture can change significantly over short periods. The treatment process will either have to have rapid response to composition changes or will have to be very forgiving regarding excursions.

The question of site selection for storage of wastes is dependent on a variety of factors, particularly geography. For rural areas where real estate is available, use of ponds (with impermeable liners if necessary) should be acceptable. Dewatering, compaction, or fixation might be justified if the trade-off in cost for transportation to an alternate nearby site offsets the value of adjacent land. For urban areas, nearby sites simply may not be available. In these cases dewatering may be essential to avoid excessive transportation costs and fixation may be required for permission to dump, particularly in conjunction with sanitary landfill practice. It has been suggested that waste materials be hauled back to the quarry from which the limestone came or to the hole where the coal used to be. In theory, this concept sounds good but in practice, the logistics may be virtually impossible. It may be more practical to improve land surface features by systematic land reclamation or development, provided that stabilization is the only alternative.

FOR RECOVERY PROCESSES--IS THE MARKET RELIABLE FOR CONTINUOUS PRODUCTION OF VARYING AMOUNTS OF A BYPRODUCT AND WHAT HAPPENS IF THE PIPELINE CLOGS?

It probably is not fair to jump 10 to 15 years into the future and conclude that the supply of sulfur products exceeds the demand. During a period of technology adoption, when the supply of recovered products is small compared to the total market, the incremental production can probably be integrated into growth markets with minimum impact, particularly if an established distributor serves as a broker. Variations in production volume from the recovery operation could be compensated by the flexibility of conventional sources. TVA has recently completed a hypothetical sulfuric acid marketing study for EPA based on the TVA system.[4] As a greater share of the total market is supplied from variable sources, the ability of the shrinking basic production to absorb the swings will diminish. On the other hand, multiplicity of recovery sources should stabilize the short-range supply and seasonal swings would cause the biggest problem. The net effect would be to downgrade the value of recovery products so that reserve capacity from conventional sources could be maintained to supply the peak demands; in other words, the cost of turndown of backup facilities would have to be deducted from the value of recovered products in order to stabilize price. This is obviously an oversimplification because where different companies in different industries are involved, coordination is difficult; industry-wide distribution strategies would be required. The situation where the supply from abatement sources approaches the annual demand would probably require an impractical amount of standby capacity and the only alternative would be unprecedented reserve storage, a costly option that needs definition. By the time that production of recovered sulfur products exceed the total demand, the value will reach a level consistent with the least cost for disposal. As the value decreases, new markets may develop and the total demand is likely to grow.

A very real concern is the need to continue production even if there is no market, at any price. An obvious answer is to bypass the desulfurization system and the circumstances for exercising this option should be defined. Flexibility to convert a recovery system to a throwaway type is a desirable feature, although the rational that led to use of recovery in the first place would probably complicate this consideration. However, for short-term interruptions waste disposal might be feasible if not practical. For processes that make sulfuric acid, the acid could be neutralized with limestone and discard gypsum. Solution scrubbing systems could be converted to a double alkali process. Processes producing elemental sulfur would fare best because the product could probably be stored indefinitely. These manipulations would play havoc with sinking fund projections, but they would provide for continued power generation.

ARE THE RULES GOING TO CHANGE?

The regulations that apply to air quality are defined more clearly than water and solid waste considerations and even they are still being debated. It is impossible to intelligently evaluate alternative processes when reliable guidelines for all effluent streams are not available. For example, selection of a throwaway system as the least cost method on the basis that waste disposal by ponding is acceptable might be a poor choice if subsequent solid waste regulations required stabilization. It would be similarly unfortunate if a process to produce elemental sulfur were chosen to minimize the impact of market uncertainties and later regulations prohibited open-pile storage.

Regulatory organizations need to consider the interactions of air, water, and solid waste control so that efforts to solve one problem do not create another; economics of compliance must take into account the total regulatory requirement.

WHAT IS THE CHEAPEST WAY OUT?

Separation of the cost elements associated with waste disposal and recovered product distribution is difficult and direct comparison of results could be misleading. The most effective way to evaluate the overall process economics is to compare the lifetime operating costs including amortization of the investment.

An earlier paper[5] in this symposium provided detailed investment and operating economics for five processes including both throwaway and recovery methods. As an example of the effect of disposal alternatives on cost, use of an onsite, unlined pond (no thickener) with clarified liquor recycle contributed approximately 7% of the total operating cost; including an impervious liner increased the cost to about 12% of the total. Offsite disposal costs (including facilities for filtration) were estimated to be approximately 10% higher than costs for onsite ponding. Chemical fixation (at an assumed cost of $10/ton of dry solids) and disposal offsite would be approximately 25% higher than onsite ponding.

Credit for sale of recovered products does not constitute a major reduction in operating costs; revenues at a price equivalent to $25 per short ton S, would reduce the lifetime operating costs less than 10%.

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LIME/LIMESTONE SLUDGE DISPOSAL - TRENDS IN THE UTILITY INDUSTRY

by

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ABSTRACT

This paper is an evaluation and summary of the present state of the art and future trends in the ultimate disposal of calcium-sulfur sludges from utility flue gas desulfurization processes. Twelve full-scale utility plants currently have the potential to generate calcium-sulfur sludges at the annual rate of about 2.5×10^6 metric tons (50 percent moisture). It is estimated that by 1980, lime/limestone scrubbing systems may generate as much as 120×10^6 metric tons of sludge (50 percent moisture) annually. Thus, the major problem in the application of lime/limestone scrubbing technology is the disposal of the large quantities of sludge. Other attendant problems are associated with the physical and chemical characteristics of the sludge. Physical characteristics influence markedly the land use of the disposal site. Chemical characteristics are strongly related to water pollution problems. Before final disposal, the scrubber sludges may be subjected to various treatments which will change their physical and chemical characteristics in order to effect an environmentally acceptable disposition. Depending on economics and local conditions, utilities may practice ponding only, or a combination of ponding and/or other mechanical pretreatment processes. Ponding without pretreatment is practiced in regions where there is relatively cheap land and/or abundant solar energy to aid evaporation. Clarification and vacuum filtration are common in regions with a high land cost and a wetter and colder climate. Current popular final disposal methods adopted by utility companies are ponding and landfill. Disposal through utilization is not yet practiced on full-scale installations, but the technical feasibility of various uses has been demonstrated by some research groups. However, most have so far proven economically unattractive.

LIME/LIMESTONE SLUDGE DISPOSAL - TRENDS IN THE UTILITY INDUSTRY

BACKGROUND

In response to the need for up-to-date, factual information on the treatment of stack gas for pollution control, Battelle-Columbus began a study focused on this subject in January, 1974. The purpose of this effort was to (1) establish a mechanism to collect installation and operating data, (2) analyze these data, and (3) distribute the resulting reports to management personnel concerned with the problem of SO_2 in stack gas.

The original program was underwritten by the Electric Power Research Institute. Additional work is being supported by the American Petroleum Institute, and a number of individual companies interested in both utility and industrial boilers. Battelle-Columbus is actively seeking additional support from other companies for this very significant group program.

The program comprises seven tasks. In brief, these are:

1. Survey installations in North America now using SO_2 control devices
2. Establish an information and analysis center for information on stack gas control
3. Prepare topical reports on subjects of importance to members of the group
4. Survey overseas installations of SO_2 control devices
5. Conduct laboratory studies on problems related to stack gas pollution control
6. Contact vendors of SO_2 control devices to obtain information on operating experience
7. Conduct review meetings.

One of the topical reports prepared is on the disposal of sludge from lime/limestone scrubbing processes. This effort will form the basis for the current presentation.

INTRODUCTION

The United States Clean Air Act of 1970 requires stationary combustion sources to control SO_2 emissions. The shortage of low-sulfur fuels has increased the importance of stack-gas cleaning to meet SO_2 emission regulations. A major division in SO_2 removal technologies is between recovery of SO_2 in useful form and formation of a solid waste. Most throwaway processes utilize limestone or lime as a raw material because of their relatively low cost and widespread availability, as well as the relative insolubility of the waste products. However, the use of lime/limestone processes to control SO_2 emissions produces large quantities of calcium-sulfur sludges. The physical and chemical characteristics of these sludges create serious disposal problems with regard to land use and water pollution.

PROCESS PARAMETERS AFFECTING SLUDGE CHARACTERISTICS

There are currently about a dozen full-scale demonstration projects for SO_2 control operating on utility boiler stack gas where calcium-sulfur sludges are produced. These processes can be classified as (1) limestone injection, (2) tail-end limestone scrubbing, (3) lime scrubbing, and (4) alkali scrubbing with calcium regeneration (double alkali process). Table 1 presents a summary of utility plants generating sludges, together with selected parameters that tend to influence sludge characteristics.

Limestone injection into the boiler has fallen into disfavor because of operating problems such as abnormal slagging, increased erosion in the boiler, and plugging in the scrubber. Plans by the utilities call for the three limestone injection demonstration plants still operating to be converted to tail-end limestone scrubbing.

Table 1 SELECTED OPERATING PARAMETERS FOR SLUDGE-PRODUCING SO_2 SCRUBBERS

Facility	Boiler Capacity, MW	Nominal Sulfur Content of Coal, wt. percent	Nominal Ash Content of Coal, wt. percent	Primary Method of Particulate Control	Method of SO_2 Control	Stoichrometric Ratio, moles Ca/mole SO_2 Removed	SO_2 Removal Efficiency, percent	pH Range in Scrubber	Approximate Mole Ratio of Oxygen to SO_2 in Gas to Scrubber
Kansas Power & Light-Lawrence 4	125	3.8	12	Marble bed	Limestone injection-wet scrubbing	1.15	60	9.0-5.3	20
Kansas Power & Light-Lawrence 5	400	3.8	12	Marble bed	Limestone injection-wet srrubbing	1.15	60	9.0-5.3	20
Kansas City Power & Light-Hawthorn 3	125	3.0	11	Marble bed	Limestone injection-wet scrubbing	1.2	70	9.0-5.0	20
Kansas City Power & Light-Hawthorn 4	140	3.0	13	Marble bed	Tail-end limestone scrubbing	1.5	70	5.5-4.5	20
Commonwealth Edison-Will County 1	165[b]	3.5	15	Venturi	Tail-end limestone scrubbing	1.5	85	5.9-5.7	40
City of Key West-Stock Island	42[c]	2.0	0.04	Mechanical collector	Tail-end limestone scrubbing	5.0	70	7.5-6.5	30
Kansas City Power & Light-La Cygne	820[b]	5.3	22	Venturi	Tail-end limestone scrubbing	1.9	80	6.0-5.6	30
Arizone Public Service-Cholla	125	0.5	10	Flooded disc srubber	Tail-end limestone scrubbing	1.0	90	6.3-5.2	100
Louisville Cas & Electric-Paddy's Run	70	3.7	14	Electrostatic precipitator	Lime scrubbing[f]	1.0	90	9.0-5.3	30
Dusquesne Light-Phillips[a]	180				Lime scrubbing				
Southern Califronia Edidon-Mohave 2	160[d]	0.4	10	Electrostatic precipitator	Lime scrubbing	1.0	90	9-5	300
General Motors-Parma[a]	32[e]				Double alkali process				

(a) Not yet visited.
(b) Cyclone boiler.
(c) Boiler fired with Bunker C fuel oil.
(d) 20 percent of gas flow from 790 MW unit.
(e) Four stoker-fired boilers.
(f) Carbide sludge.

The double alkali process attempts to circumvent plugging and scaling problems in the scrubber. By scrubbing the SO_2 with soluble sodium salts and reacting the scrubber effluent with lime, calcium-sulfur compounds are produced for waste disposal, while yielding a solution of NaOH and Na_2SO_3 for recycle back to the scrubber. Although this process has not been applied to a utility boiler, it is currently in operation on an industrial boiler.

The factors influencing sludge characteristics include size of power plant, type of boiler, type of fuel burned, sulfur and ash content of fuel, method of fly ash removal, method of SO_2 control, stoichiometric ratio of calcium to SO_2 removed, and SO_2 removal efficiency. It is speculated that the pH range in the scrubber and the mole ratio of oxygen to SO_2 in the gas entering the scrubber may also affect sludge characteristics. The size of the power plant affects the total quantity of sludge produced. The type of fuel burned, sulfur content of the fuel, and SO_2 removal efficiency affect the quantity of calcium-sulfur compounds in the sludge. The type of boiler, ash content of the fuel, and the method of fly ash removal affect the fly ash content of the sludge. In some cases, most of the fly ash is removed in an electrostatic precipitator ahead of the scrubber so that it can be kept separate from the sludge. In other cases, the fly ash is removed in either the same scrubber as the SO_2 or in a Venturi-type scrubber ahead of the SO_2 scrubber. The quantity of fly ash that is removed by wet scrubbing in conjunction with SO_2 removal ends up in the sludge. The stoichiometric ratio of calcium to SO_2 removed affects the $CaCO_3$ content of the sludge. A mole ratio in excess of one means that unreacted limestone leaves with the scrubber effluent. If the reactant is lime, any excess presumably reacts with CO_2 in the flue gas to form $CaCO_3$.

The calcium-sulfur compounds present in the sludge are calcium sulfite and calcium sulfate. The relative amount of each depends upon the level of oxidation in the scrubber system. The factors that appear to affect oxidation include the amount of fly ash removed in the scrubber, the pH range in the scrubber, and the mole ratio of oxygen to SO_2 in the gas entering the scrubber. The method of SO_2 control affects the pH range in the scrubber (limestone slurries are lower in pH than lime slurries). Also, in the double alkali process, some sodium salts can appear in the sludge.

Table 2 summarizes the dry sludge production rate on an hourly basis and the approximate composition of the sludge for the full-scale plants currently in operation. The data listed in this table are best estimate calculations based on information obtained during plant visits. The amount of water in the sludge influences the total tonnage. The scrubber effluents contain a solids content in the range of 5 to 15 percent by weight and must be dewatered to a point where sludge disposal can be economically feasible and ecologically acceptable. The sludge production rate on a yearly basis depends upon plant capacity factor and availability of the SO_2 control system. Assuming a 65 percent capacity factor for each plant and 90 percent availability for each SO_2 control system, the plants listed in Table 2 have the potential to generate sludges at the rate of about 2.5×10^6 metric tons (50 percent moisture) annually. It is estimated that by 1980 lime/limestone scrubbing systems may generate as much as 120×10^6 metric tons (50 percent moisture) annually.[1]

The limestone injection systems produce a sludge consisting mainly of fly ash and calcium sulfate with some calcium sulfite and a little calcium carbonate. This composition occurs because the fly ash is removed in the same marble bed scrubber as the SO_2, and the presence of fly ash appears to promote oxidation. The calcium carbonate in the sludge results from a stoichiometric ratio of about 1.2. The sludge composition for the tail-end limestone scrubbing systems varies greatly with process parameters. The fly ash content for the Stock

Table 2 CHACTERISTICS OF SLUDGE FROM OPERATING SO_2 SCRUBBERS

Facility	Rate (dry basis), metric tons/hr	Sludge Composition (dry basis), wt. percent				Estimated Solids Content of Dewatered Sludge, wt. percent
		$CaSO_3 \cdot 1/2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	Flyash	
Lawrence 4	10.7	10	40	5	45	50
Lawrence 5	34.4	10	40	5	45	50
Hawthorn 3	12.4	20	25	5	50	40
Hawthorn 4	15.4	17	23	15	45	40
Will County 1	17.5(b)	50	15	20	15	35
Stock Island	2.4	20	5	74	1(c)	50
La Cygne	12.5	40	15	30	15	35
Cholla	3.1	15	20	0	65	50
Paddy's Run 6	5.3	94	2	0	4	40
Phillips(a)						
Mohave 2	1.5(b)	2	95	0	3	65
Parma(a)						

(a) Not yet visited.

(b) Prior to stabilization.

(c) Mainly unburned carbon.

Island sludge is very low because it is an oil-fired boiler, while calcium carbonate content is high because of the very high stoichiometric ratio of calcium to SO_2 removed. The Will County and La Cygne sludges contain less fly ash than might be expected because cyclone boilers produce less fly ash than other types of boilers. The Cholla sludge does not contain any calcium carbonate because the stoichiometric ratio is one. The concentration of calcium sulfate is greater than calcium sulfite in this sludge because of the presence of fly ash and the high ratio of oxygen to SO_2 entering the scrubber. This latter effect is a direct result of burning low-sulfur coal.

The two lime scrubbing installations visited (see Table 1) present an interesting contrast. Both installations remove fly ash in electrostatic precipitators ahead of the SO_2 scrubbers and both scrubbers probably operate in the same pH range. The Paddy's Run scrubber is a two-stage marble bed and the Mohave scrubber is a horizontal spray chamber with four spray headers in series. The sludge at Paddy's Run is practically all calcium sulfite, presumably because the relatively high pH level in the scrubber prevents oxidation by keeping sulfite out of solution. However, the sludge at Mohave is practically all calcium sulfate. The low-sulfur coal and high excess air in this instance cause a very high ratio of oxygen to SO_2 in the inlet gas to the scrubber.

WATER POLLUTION AND LAND USE PROBLEMS

The tendency of sludge to pollute surface and groundwater is largely dependent on its chemical composition. Sludges from lime/limestone SO_2 control processes generally contain $CaSO_3 \cdot \frac{1}{2} H_2O$, $CaSO_4 \cdot 2H_2O$, $CaCO_3$, and fly ash. Other minor compounds (e.g., sodium, ammonium, and magnesium salts) may be present because they occur in the lime or limestone, in makeup water, or are purposely introduced into the system as in the double alkali process. The composition of fly ash varies greatly with coal type, but generally consists of silica, alumina, and iron oxides with lesser amounts of alkaline earth and alkali metal oxides and trace amounts of heavy metal oxides. However, the fly ash content of the sludge would not be expected to present a greater disposal problem than that of fly ash alone which has been ponded and landfilled for many years. On the other hand, the $CaSO_3 \cdot \frac{1}{2} H_2O$ content of the sludge could pose problems because of the chemical oxygen demand of sulfite ions.

The physical and chemical characteristics of the sludge influence the amount of land required for disposal and future use of the ponded area. The pond volume requirement for lime/limestone sludge is larger than that required for fly ash disposal because of the larger packing volumes of the former. Most fly ash settles compactly requiring only about 0.6 m^3 per metric ton of dry solids (20 ft^3 per ton) while scrubber sludges appear to have packing volumes between 1.4 and 2.3 m^3 per metric ton of dry solids (45 and 75 ft^3 per ton). The ratio of calcium sulfite to calcium sulfate in the sludge is significant to the packing volume. Sulfite presents a more significant land use problem than sulfate. Sulfites tend to crystallize in small, thin platelets which settle to a loose bulky structure that may occlude a relatively large amount of water. The net result is to increase the land required for disposal. For example, the Paddy's Run sludge which consists mainly of calcium sulfite contains only 40 percent solids after vacuum filtration, while the Mohave sludge which consists mainly of calcium sulfate contains 65 percent solids after settling in a clarifier. For a typical 1,000 MW coal-fired station, the disposal of lime/limestone sludge will require between 12.2 to 24.3 hectares (30 to 60 acres) per year ponded to a 3-meter (10-foot) depth. The lower figure represents the area required for sulfate sludge, while the higher figure represents the area required for sulfite sludge.

Currently, ponding and landfilling are the only methods practiced by utilities for the disposal of lime/limestone sludges. However, the problems associated with these disposal methods are becoming increasingly difficult. These problems are related to finding suitable disposal sites close to the plant and the high cost of removal to a disposal site away from the plant. The magnitude of the problems tend to be site specific. In the case of Key West or Will County, there is little or no land available adjacent to the plant while at Lawrence or La Cygne, there is abundant available land adjacent to the plant. The land used for waste disposal may be structurally unstable and aesthetically objectionable. If the disposal site is not available for future land use, the land loses its production capacity. Therefore, additional sludge treatment by chemical fixation and alternative disposal processes through commercial utilization are being developed. Unfortunately, chemical fixation can significantly increase the cost of waste disposal, and limited utilization options are available. Thus far, the sludge by-products are too expensive to compete with natural sources of the same or similar material.

CURRENT SLUDGE PROCESSING TECHNIQUES

The present status of sludge processing and disposal by utilities is in the development stage, with wide variations in technique being practiced at different locations. In most cases, economics have been the controlling factor so that the easiest and cheapest method of sludge treatment and disposal has usually been selected. Therefore, the disposal method adopted has always been a throwaway method--ponding or landfilling. Table 3 provides a summary of the sludge disposal systems currently in use at plants employing lime/limestone scrubbing. The particular processes selected by a utility are dictated as stated earlier by site location and, to a lesser extent, environmental pressures, in addition to economics.

Table 3 CURRENT SLUDGE DISPOSAL PRACTICES IN THE UTILITY INDUSTRY

			Pretreatment Method						Ultimate Disposal Method		
Facility	Location	Effluent Management	Oxidation	Clarifier	Vacuum Filter	Centifuge	Pond	Chemical Fixation	Ponding	Landfill	Utilization
Lawrence 4	Lawrence, Kansas	Closed loop					X		X		
Lawrence 5	Lawrence, Kansas	Closed loop					X		X		
Hawthorn 3	Kansas City, Missouri	Open loop(a)		X			X		X		
Hawthorn 4	Kansas City, Missouri	Open loop(a)		X			X		X		
Will County 1	Lockport, Illinois	Closed loop		X				X(d)		X	
Stock Island	Key West, Florida	Open loop					X		X		
La Cygne	La Cygne, Kansas	Closed loop					X		X		
Cholla	Joseph City, Arizona	Open loop(b)					X		X		
Paddy's Run	Louisville, Kentucky	Closed loop		X	X					X	
Phillips	South Heights, Pa.	Closed loop		X			X	X(e)		X	
Mohave 2	South Point, Nevada	Closed loop(c)		X			X	X(e)	X	X	
Parma	Parma, Ohio	Closed loop		X	X					X	

(a) Closed loop with respect to clarifier and open loop with respect to pond.
(b) Solar evaporation.
(c) Aided by solar evaporation.
(d) Chicago Fly Ash method.
(e) Dravo method.

PRETREATMENT

Pretreatment refers to those processes to which the sludge is subjected prior to ultimate disposition. There are three broad approaches to pretreatment: (1) oxidation of calcium sulfite to calcium sulfate, (2) reduction of moisture content by various dewatering schemes, and (3) chemical/physical fixation processes. It is possible for a power plant to employ one or more approaches depending upon the desired method of ultimate disposal and the economics involved; however, dewatering is almost always a necessity. Oxidation improves sludge compaction and can produce a salable by-product (gypsum); dewatering provides reduced sludge volumes to handle, manage, or transport to the disposal site; fixation processes convert the sludge into a relatively nonleachable stabilized material.

Oxidation. The oxidation of the small gel-like sulfite crystals in the sludge to the larger sulfate crystals improves agglomeration and compaction and, thus, dewaterability of the sludge. No operating lime/limestone system in the United States practices intentional oxidation. This is in contrast with the Ando (1973)[2] account of the Japanese systems where oxidation is practiced extensively in order to produce gypsum for sale. However, the supply and demand situation for gypsum is much different in Japan than in the United States. Incidental oxidation occurs in lime/limestone scrubber systems because of oxygen present in the flue gas and because of contact with air in the recirculation tank, clarifier, and pond. Oxidation appears to be enhanced by low pH, the presence of fly ash in the scrubber, and a high ratio of oxygen to SO_2 in the flue gas entering the scrubber.

Dewatering. The scrubber effluent must be processed to settle the thixotropic suspension and dewater the solids prior to ultimate disposition. The solids are recovered and concentrated, while the clarified liquid effluent is recirculated (closed-loop operation), or discharged to a receiving body of water (open-loop operation). In some cases, the scrubber effluent is evaporated in the sun (open-loop operation). Open-loop operation increases the dissolved solids content of the receiving body of water, except in the case of solar evaporation, but it reduces plugging and scaling problems in the scrubber system by permitting more fresh water makeup for washing critical components such as the mist eliminator. However, open-loop operation is not permitted in most locations. The plants currently operating in the open-loop mode are Hawthorn, Stock Island, and Cholla. Hawthorn is actually operating in what may be described as semi-open loop since the clarifier overflow is recycled but the pond overflow is discharged to the Missouri River. The pond overflow at Stock Island is discharged to the Atlantic Ocean while the pond water at Cholla is subjected to solar evaporation. Mohave operates in the closed-loop mode but there are times when no recycle of pond water is necessary because of solar evaporation.

There are many possible schemes available for sludge dewatering. However, only three schemes are currently used at full-scale lime/limestone scrubber installations. These include ponding (or clarification) only, clarification followed by ponding, and clarification followed by a vacuum filtration. Dewatering by ponding only is shown schematically in Figure 1 and is practiced at Lawrence, Stock Island, La Cygne, and Cholla. At Lawrence and La Cygne, the relatively high solids content of the recirculating slurry (9 to 10 percent at Lawrence and 15 to 20 percent at La Cygne) is kept in suspension by high power mixers and baffles. A bleed stream from the recycle tank is sent to the sludge pond and the pond overflow is recycled to the scrubber system. At Stock Island, a slip stream from the scrubber hoppers goes to two settling ponds and clarified effluent is discharged to the sea through overflow pipes; sea water is used in the scrubber system because fresh water is very expensive at this location. At

Cholla, a bleed stream from the scrubber recirculation tank is sent to two sludge storage tanks; the tanks are emptied to an existing ash pond about once per shift and the water inflow to the pond is lost by evaporation. Ponding is not a problem in Kansas and Arizona where land is available, but it is a very serious problem in Key West where the entire island is only five square miles in area and the sludge ponds have a useful life of only 21 days.

The dewatering system of a clarifier followed by a pond is shown schematically in Figure 2. The use of a clarifier ahead of the pond tends to decrease the pond area required. The clarifier surface area varies from 1 to 10 m^2/metric ton/day (10 to 100 ft^2/ton/day) depending on the settling characteristics of the sludge. This method of dewatering is practiced at Hawthorn, Phillips, and Mohave. The clarifier used at Hawthorn is shown in Figure 3.

The dewatering system of a clarifier followed by a vacuum filter is shown schematically in Figure 4 and is practiced at Paddy's Run and Parma. The addition of a vacuum filter is a great aid in reducing the moisture content of the sludge. At Paddy's Run, the clarifier bottoms contain 23 percent solids and are filtered to produce a cake containing 40 percent solids for landfill. This filter is shown in Figure 5. The filtrate is returned to the clarifier.

Alternatively, a centrifuge can be used instead of a vacuum filter. Although none of the plants listed in Table 3 use a centrifuge, it is being used at the Shawnee pilot plant and will be tried at the limestone scrubbing installation on Mohave Unit 1. The use of a centrifuge can effect a high degree of dewatering at the expense of a

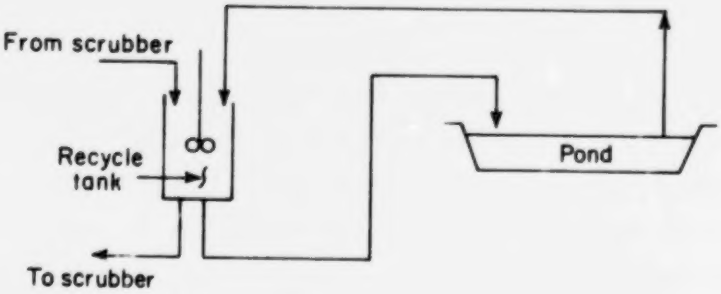
From scrubber
Recycle tank
Pond
To scrubber

Figure 1 Sludge dewatering by ponding.

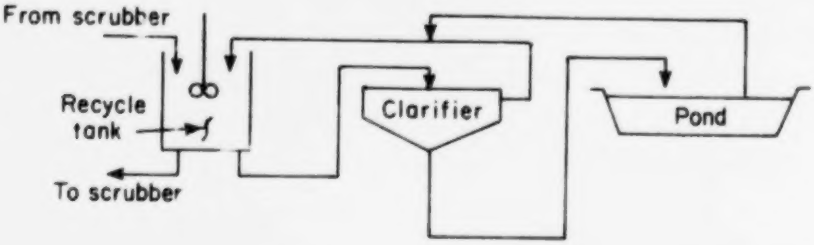
From scrubber
Recycle tank
Clarifier
Pond
To scrubber

Figure 2 Sludge dewatering by clarification and ponding.

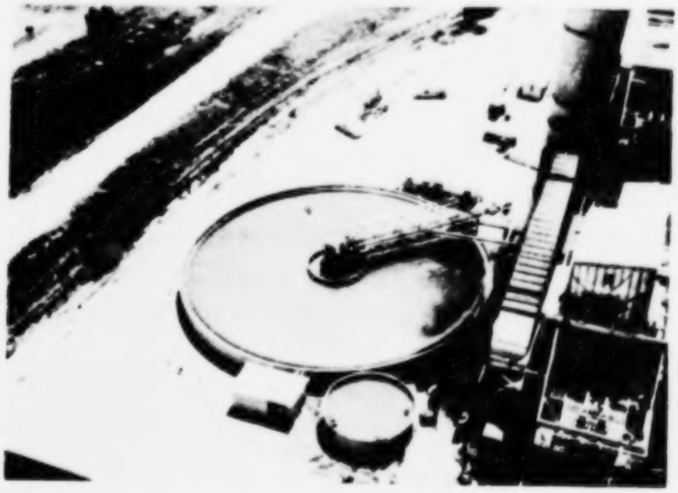

Figure 3 Hawthorn clarifier.

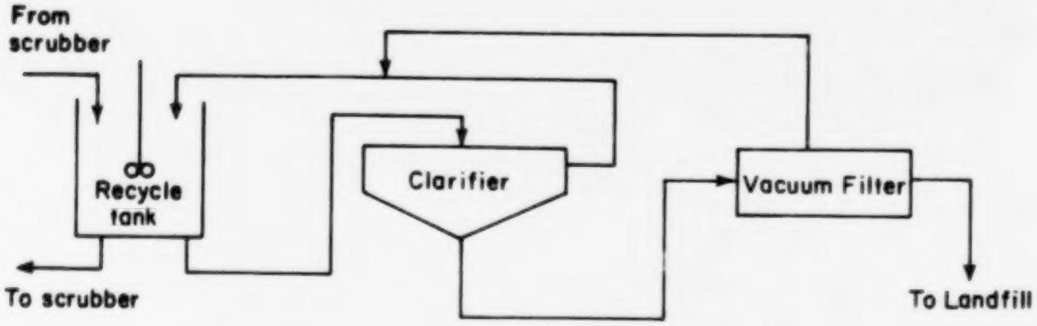
From scrubber
Recycle tank
Clarifier
Vacuum Filter
To scrubber
To Landfill

Figure 4 Sludge dewatering by clarification and filtration.

Figure 5 Paddy's Run filter.

relatively high power consumption. Also, the centrifuge internals may be subjected to undue wear because of erosion.

Chemical Fixation. Chemical fixation stabilizes the sludge by changing its physical and chemical characteristics so that it can be landfilled or utilized as a by-product. Currently, Will County, Phillips, and Mohave are using chemical fixation processes. At Will County, the fixation is handled by the Chicago Fly Ash Company. The clarifier bottoms, which are about 35 percent solids, are treated with 10 percent lime and 20 percent fly ash based on dry solids in a redi-mix truck. The sludge is mixed while it is being hauled one mile for dumping in a clay-lined basin where it sets up in a few days. Phillips and Jones (1973)[3] have reported the Chicago Fly Ash process to cost $16.50/metric ton ($15/ton) on a dry solids basis.

Sludge stabilization is going to be studied in an advanced program at the Shawnee test facility under the direction of the Aerospace Corporation. Three different proprietary processes will be studied--Dravo, IU Conversion Systems, and Chemfix. There will be a large pond for untreated sludge and three small ponds for treated sludge (one for each process). Each pond will have a leachate well and a groundwater well to monitor any groundwater contamination.

ULTIMATE DISPOSAL

Utilities can finally dispose of the scrubber sludge by ponding, landfilling, or utilization. Currently, ultimate disposal is about evenly divided between ponding and landfilling with no utility producing a by-product for utilization. Ponding can be used to dispose of untreated scrubber effluent, dewatered sludge, or chemically fixed sludge. Untreated scrubber effluent is ponded at Key West, Lawrence, La Cygne, and Cholla; dewatered sludge is ponded at Hawthorn; and chemically fixed sludge is ponded at Mohave. Typical pond disposal sites at Key West and Lawrence are shown in Figures 6 and 7, respectively. The significance of these figures is the wasted land area occupied by the ponds and the cracking of the pond surface at Key West. Thus far, there has not been any study of pond seepage or leaching at full-scale scrubber installations.

Landfilling of scrubber sludges requires dewatering and stabilization. Dewatering improves handling characteristics and stabilization improves the load-bearing strength of the landfilled site. At Paddy's Run, a filter cake of calcium sulfite containing 40 percent solids is trucked to a borrow pit where it is landfilled together with fly ash. Now and then the sludge and fly ash are mixed with a bulldozer. Presumably the fly ash aids in stabilizing the sludge. At Will County, stabilized sludge is dumped in a seven acre, clay-lined basin, as shown in Figure 8. As far as is known, there have not been any leachate studies or load-bearing studies at either site. Thus far, Commonwealth Edison has not found a private landfill operator willing to take the waste material.

Utilization of scrubber sludges as building material has been demonstrated as technically feasible. However, economic factors have discouraged utilities in the United States from practicing any of the utilization approaches in a full-scale application. In 1972, sludge from the Lawrence site was transported to Dulles Airport and mixed with fly ash for use as a parking lot pavement. This test resulted in the sponsoring of further research by the Federal Highway Department. The first large-scale application of sludge utilization will be at the limestone scrubber installation at Mohave Unit 1 where IU Conversion Systems will convert the sludge into a building material.

Figure 6 Key West pond.

Figure 7 Lawrence pond.

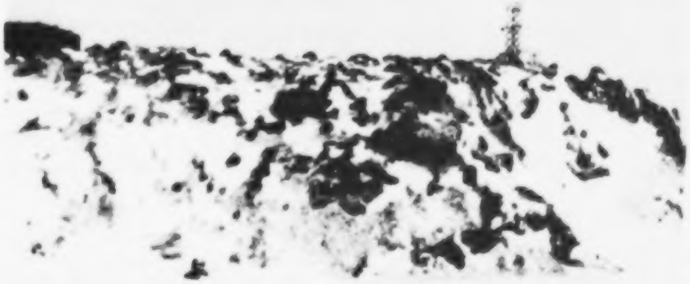

Figure 8 Will County sludge basin.

CONCLUSIONS AND RECOMMENDATIONS

The disposal of sludge is probably the major problem in the application of lime/limestone scrubbing technology. The dozen plants that are employing this technology have tried to dispose of the sludge in the most expedient manner. Thus far, the success of the sludge disposal operation has largely depended on plant location. In areas where abundant land adjacent to the plant is readily available, disposal by ponding appears to be an adequate solution. However, in other locations the sludge disposal problem remains unresolved. Chemical fixation and landfill may provide the answer; or perhaps by-product utilization is the way to proceed. The advanced program at the Shawnee test facility to study sludge stabilization, pond leaching, and groundwater contamination should prove to be extremely valuable. However, more extensive work at existing full-scale installations practicing either ponding or landfilling would appear worthwhile. It would also be highly desirable to encourage further development of sludge by-products.

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ENVIRONMENTALLY ACCEPTABLE DISPOSAL OF FLUE GAS DESULFURIZATION SLUDGES: THE EPA RESEARCH AND DEVELOPMENT PROGRAM

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CONTENTS

Page

1.0 Introduction 891

2.0 Summary 891

3.0 Definition of the Problem 896

4.0 Current Approaches to Disposing of or Utilizing Scrubber Sludge Materials 907

5.0 Current EPA R and D Programs 912

6.0 References 926

ABSTRACT

A recent assessment has been made concerning the environmental and economic factors associated with disposal of sludge from non-regenerable flue gas desulfurization (FGD) processes. Lime/limestone scrubbing systems are expected to comprise the majority of FGD process installations on power plants through 1980, producing approximately 35,000,000 short tons (dry, excluding coal ash) of sludge annually by 1980. This compares to an expected coal ash production of about 83,000,000 tons (dry) annually by 1980. Since uncontrolled disposal of raw (untreated) sludge presents potential water pollution and land reclamation problems, environmentally sound disposal techniques (e.g., chemical fixation) need to be employed. Most of the chemical constituents of concern originate in the coal, indicating that FGD processes provide a multi-pollutant control capability. Because of considerable variation in FGD system applications, FGD sludge properties, and electric utility sludge disposal approaches, EPA has undertaken additional research and development efforts to increase the environmental and cost effectiveness of current sludge disposal techniques. Several programs are underway at National Environmental Research Centers (NERCs) in Research Triangle Park (RTP), N.C.; Cincinnati, Ohio; and Corvallis, Oregon. The most broadly-based program is a NERC-RTP contract with The Aerospace Corporation. Initiated during late 1972, this effort includes: quantification of potential water pollution and land reclamation problems; technical and economic evaluation of currently available treatment/disposal techniques; and support of an EPA field study of sludge disposal at TVA's Shawnee Steam Plant. Results to date have verified the need for environmentally sound disposal techniques; the most practical are landfilling of chemically fixed sludge and disposal of untreated sludge in ponds lined with an impervious material such as clay, plastic, or rubber. Disposal cost estimates range from $2 to $9 per ton (wet, 50 percent solids). Although less expensive than fixation, ponding may cause subsequent land reclamation costs to be incurred. The Shawnee field study, which includes evaluation of the Chemfix, Dravo, and IU Conversion Systems sludge fixation processes, was initiated in September 1974. In mid-1974, NERC-Cincinnati initiated an interagency agreement with the U.S. Army Corps of Engineers to study the leachability and durability of raw and chemically fixed hazardous industrial wastes and FGD sludges. Also in mid-1974, NERC-Cincinnati initiated an interagency agreement with the U.S. Army Materiel Command to study migration of chemical constituents from industrial and FGD sludges through soils. NERC-Corvallis has issued a grant to Aerospace to ascertain the water pollution and reuse potential of treated and untreated scrubber liquors; the study will be completed in January 1975.

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1.0 INTRODUCTION

A major problem inherent in any flue gas desulfurization (FGD) system is the necessity for disposing of or utilizing large quantities of a sulfur product. Application of FGD systems in the United States is accelerating; the majority of these are lime/limestone wet scrubbing systems producing a sludge by-product. Because of environmental, economic, and other concerns related to the disposition of this FGD sludge, there have been considerable research, development, and demonstration activities, both in the public and private sector. In this paper, the FGD sludge disposition problem is defined and quantified, and efforts to solve the problem are discussed. In the discussion of these efforts, emphasis is placed on U.S. Environmental Protection Agency (EPA) research and development programs.

2.0 SUMMARY

Based on a review of sulfur oxides (SO_x) control technologies, FGD systems installed on units burning high sulfur coal is the major alternative to scarce clean fuels between now and 1980. Installation of FGD systems is presently demand-limited; regulatory pressures are expected to change this to a supply-limited situation sometime between 1975 and 1977. This situation is expected to continue through about 1980. Under these conditions, it is estimated that FGD control will most likely be installed on 90,000 Mw or about 35 percent of total estimated coal-fired utility generating capacity by 1980. Most of the 90,000 Mw capacity is expected to be controlled by lime/limestone wet scrubbing systems producing a throwaway sludge. If all of the installations are lime/ limestone systems, up to 118,000,000 metric tons/year (130,000,000 tons/year) of wet sludge including ash will be produced by 1980 (assuming limestone scrubbing, combined sludge + ash disposal, 50 percent solids).

In placing sludge production in quantitative perspective, it has been determined that approximately 346,000 metric tons (381,000 tons) of scrubber sludge and 307,000 metric tons (338,000 tons) of coal ash, on a dry basis, will be produced annually by a typical 1000 Mw coal-fired plant. This represents an increase of about 110 percent over the solid waste produced by a plant with ash particulate controls only. However, when compared to the land usage associated with a typical 1000 Mw coal-fired plant, the waste disposal area for sludge and ash is only about one percent of the total. Nevertheless the environmental impact of each individual land usage varies considerably, requiring consideration of many factors other than the relative areas involved. When compared to other solid wastes, the quantity of dry sludge (excluding ash) projected to be produced in 1980, although larger than the quantity of some wastes, is considerably less than that of others. For example, the dry sludge production rate is anticipated to be about 40 percent of the production rate of all coal ash from power plants.

In placing scrubber sludge in qualitative perspective, data have been assembled on physical and chemical properties of various scrubber sludge materials. These data show a wide variation in properties of sludges from different units. However, in general, the data indicate that raw (untreated) scrubber sludges, depending on the amount of calcium sulfite present, are difficult to dewater and have little or no compressive strength as produced. These properties present potential disposal area reclamation problems. In addition, the raw sludge liquors contain dissolved chemical species in concentrations which considerably exceed water quality criteria. These include mercury, selenium, boron, chloride, sulfate, and total dissolved solids. Most of the constituents of concern originate in the coal, indicating that FGD processes provide a multi-pollutant control capability. These problems must be addressed by the lime/limestone process user. Several approaches have been or are being investigated, including commercial utilization of the sludge and a variety of currently available sludge disposal techniques.

Technology exists for utilization of scrubber sludge in products such as mineral wool, bricks, gypsum, road base materials, artificial aggregate, and aerated concrete. However, because of major marketing inhibitions, appreciable commercial utilization of sludge is unlikely. The only important near term alternatives appear to be disposal by ponding and disposal by landfill.

Based on current and planned lime/limestone FGD system installations, utilities are using ponding and landfill disposal techniques, with and without fixation processes. The choice is usually based on environmental/economic considerations peculiar to each plant site. For this reason EPA has undertaken several programs to develop the additional information and data needed to assure more general application of sludge disposal technology and to further minimize environmental effects, at reasonable costs.

The most broadly-based EPA program relating to scrubber sludges is the National Environmental Research Center - Research Triangle Park, N.C. (NERC-RTP) study with The Aerospace Corporation. This study is designed to identify environmental problems associated with scrubber sludge disposal, to assess current sludge disposal technologies, and to make recommendations regarding alternate disposal approaches. The effort includes technical support of an EPA/TVA sludge disposal field evaluation currently underway at the TVA Shawnee Steam Plant.

In the Aerospace Corporation study, sludge samples have been analyzed from three scrubbers involving lime/Eastern coal, limestone/ Eastern coal and limestone/Western coal. (Samples from two additional scrubbers were analyzed under a NERC-Corvallis study. Results of these analyses have also been assessed as part of the NERC-RTP study.) A preliminary assessment was made with regard to any potential environmental problem that might be posed if the sludge liquors entered water supplies by comparing the liquor analyses with the EPA Proposed Public Water Supply Intake Criteria (October 1973). Based on the concentrations of several trace metals and major dissolved species (previously described) the assessment strongly indicated that environmentally sound techniques, are needed for scrubber sludge disposal.

Detailed physical characterization of various samples has also been performed under the Aerospace Corporation study. Results of the characterization have verified the water retentive nature of calcium sulfite and have quantified the effect of moisture on sludge physical properties. For example, at 65 percent solids content, sludges will support personnel, and at solids content greater than 70 percent, sludges will support heavy equipment. However, the cost of dewatering the sludge and maintaining the disposal site at the necessary degree of dryness may or may not compare favorably with the cost of an alternative disposal technique such as chemical fixation. Data from chemical fixation processors indicate that treated sludge quickly attains a compressive strength which can make the disposal site reclaimable for either structural or recreational use. Tests are currently underway in the Aerospace study to independently verify the performance of these chemical fixation techniques.

Based on available information, the best environmentally sound methods currently available for sludge disposal are landfilling of chemically fixed sludge and disposal of untreated sludge in ponds lined with an impervious material, such as clay, plastic, or rubber. Estimates from various sources indicate disposal costs of from \$2 to \$9/(short) ton for chemical fixation and from \$2.50 to \$4.50/ton for ponding, excluding possible subsequent pond reclamation costs. In a typical power plant application, a \$5/ton disposal cost would be equivalent to 1.12 mills/Kwhr.

Initial results of the Aerospace contract were reported in May 1974. A second report should be issued in mid-1975. The final report of the effort is expected to be released in late 1976.

In the EPA field study, sludges will be obtained from 10 Mw lime/limestone pilot scrubbers at the TVA Shawnee Steam Plant near Paducah, Kentucky, and will be placed into five ponds dug in the clay soil nearby. One pond will receive raw lime sludge; one pond will receive raw limestone sludge; one pond will receive lime sludge chemically conditioned by IU Conversion Systems, Inc. (IUCS); one pond will receive limestone sludge chemically conditioned by Dravo Corporation; and one pond will receive limestone sludge chemically conditioned by Chemfix (Division of Environmental Sciences, Inc.). All fixation will be performed on-site during the period October - December 1974. Each pond will have a leachate well and a ground water well. Tests will be performed to evaluate the environmental acceptability of disposal of both untreated and treated sludge in clay-lined disposal areas. Preliminary results are expected in mid-1975; a final report will be issued in late 1976.

Two programs were initiated in mid-1974 by NERC-Cincinnati to evaluate the environmental effects of FGD sludge disposal. One of these is an interagency agreement with the U.S. Army Corps of Engineers' Waterways Experiment Station in Vicksburg, Mississippi. Under this agreement, the leachability and durability of raw and chemically fixed hazardous industrial wastes and FGD sludges are being studied. Five industrial sludges and up to six FGD sludges are being obtained for the study. Results of laboratory studies are expected to be reported in mid-1975. Interim results of field studies will be reported in mid-1976; final field study results will be reported in mid-1977.

The second program is also an interagency agreement, with the U.S. Army Materiel Command's Dugway Proving Ground, Dugway, Utah. Under this agreement research is being conducted to determine the extent to which heavy metals and other chemical constituents from thirteen industrial and three FGD sludges could migrate through the soil in land disposal sites. After initial screening tests with a variety of U.S. soils, leachate column studies will be performed with two selected (best and worst) soils. Long-term permeability tests with selected clays are also planned for the FGD sludges. Results of the screening tests will be reported in mid-1975. Preliminary results of the column studies are expected to be reported in late 1975; the final results are expected to be reported in late 1976.

NERC-Cincinnati is also currently considering a full-scale FGD sludge disposal demonstration program with a utility which uses high sulfur coal.

NERC-Corvallis (Oregon) has issued a grant to Aerospace Corporation to determine the implications of open-loop or partially open-loop operation of lime/limestone FGD systems. Analyses of various sludge liquors will be performed and technologies for liquor treatment will be evaluated. These data will be used to ascertain the water pollution and reuse potential, for various plant uses, of treated and untreated scrubber liquors. The final report is expected to be issued in mid-1975.

The EPA organizations are closely coordinating the sludge disposal research and development efforts just described. These efforts represent a multi-disciplinary approach, since personnel with expertise in air pollution control (NERC-RTP), solid waste/residuals management (NERC-Cincinnati) and water treatment/water quality (NERC-Corvallis) are involved.

3.0 DEFINITION OF THE PROBLEM

3.1 Availability of Alternative SO_x Control Options

United States Department of the Interior data indicate that net electric generation by fossil-fueled power plants will increase from 1310 billion Kwhrs in 1971 to 1950 billion Kwhrs in 1980.[1] To meet this rapid increase in demand, the electric utility industry will have to consume large additional quantities of fossil fuels. The utilities will have to do this, however, without violating air pollution emission restrictions on sulfur oxides, nitrogen oxides, and particulates. Sulfur oxide restrictions require that the utilities make a choice from several alternatives. These include low-sulfur fuels, fuel cleaning and conversion, and flue gas desulfurization (FGD).

The amount of natural gas and low-sulfur fuel oil available to electric utilities will be supply-limited at least until 1980.[1] In addition, although abundant low-sulfur coal reserves exist (primarily in the Western states), availability in the near term will be hampered by the mining industry's difficulty in expanding rapidly and the high transportation costs in delivering coal to Eastern and Mid-Western regions where the greatest demand exists. Differences between Western and Eastern coal characteristics could also cause operating problems in Eastern plants.

Since low-sulfur fuel availability is inadequate, other alternatives for meeting emission restrictions must be considered. Technological developments in fuel cleaning, advanced combustion, and fuel conversion areas have been rapid in the past few years. However, since none of these schemes has advanced past the pilot plant stage, it is unlikely that any of these processes will provide a significant percentage of the low-sulfur fuel needed in this country by 1980. Therefore, the only major alternative to low-sulfur fuel between now and 1980 is flue gas desulfurization (FGD).[2] The leading FGD processes include lime/limestone scrubbing, sodium scrubbing with thermal regeneration (Wellman-Lord), magnesium oxide scrubbing, and catalytic oxidation (Cat-Ox). The lime/limestone scrubbing processes produce a throwaway product (non-regenerable processes), whereas the other three processes produce a saleable product (regenerable processes). The potential demand for these processes is examined below.

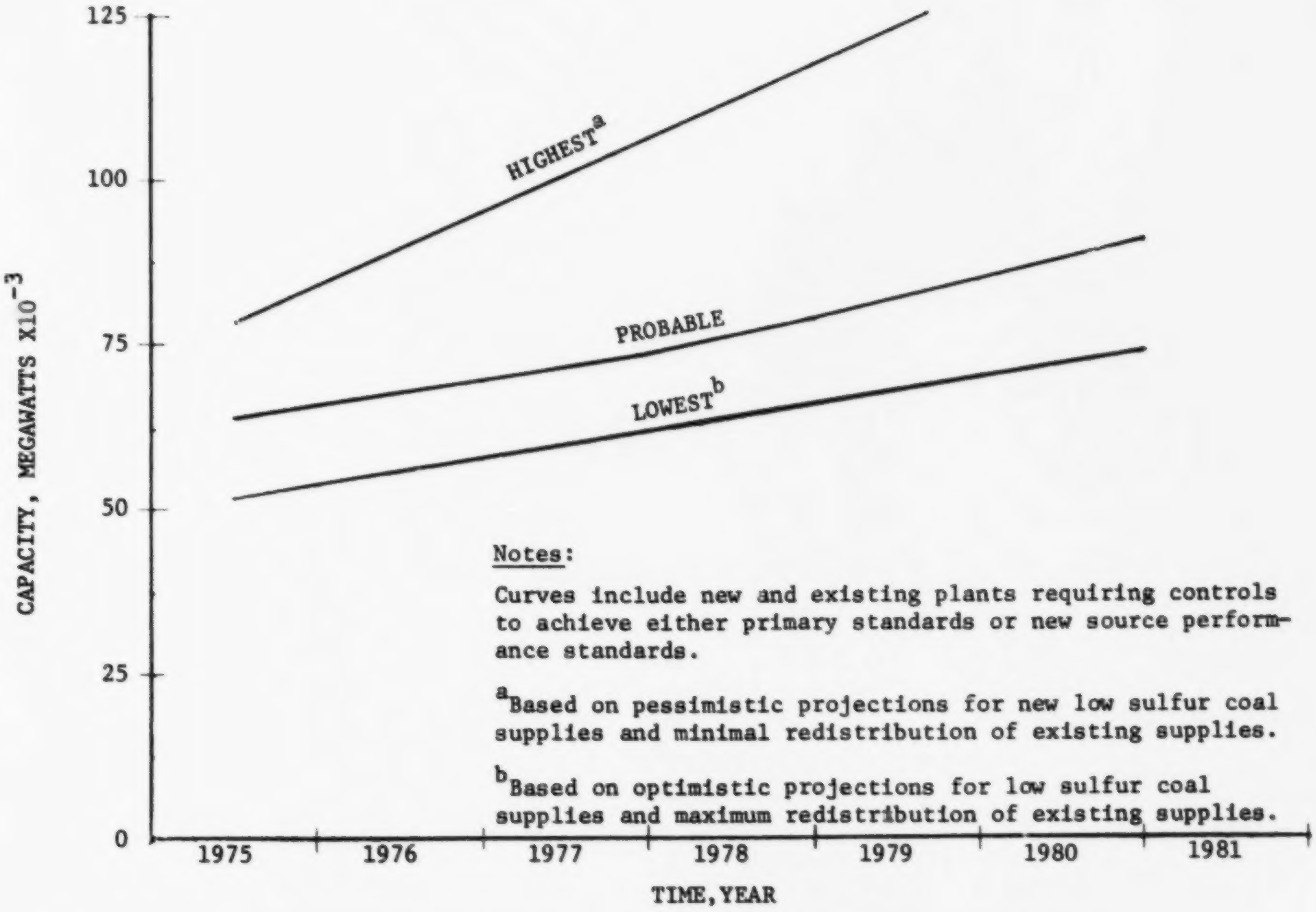
3.2 Potential Demand for Lime/Limestone Scrubbing

Installation of flue gas desulfurization systems in the utility industry is presently demand-limited and is expected to remain demand-limited through 1975. The total generating capacity controlled by the end of 1975 is projected to be no more than 10,000 Mw. (Current commitments through 1977 total about 22,000 Mw.) Because of regulatory pressures, the installation of FGD systems should become supply-limited sometime between 1975 and 1977. From 1977 to 1980 the installation of flue gas desulfurization systems will almost certainly be supply-limited. Based on regulatory pressures and expanding generating capacity coupled with a clean fuels deficit, it has been forecast that a maximum of over 130,000 Mw of installed coal-fired generating capacity will need to be controlled by FGD systems by 1980. However, the most likely demand figure by 1980 is estimated at 90,000 Mw of FGD control, or about 35% of total estimated coal-fired generating capacity. In the post-1980 period, depending on the commercial availability and viability of alternate clean fuel technologies, FGD systems could be installed to the extent that they approach demand requirements. Recent projections by EPA for the need for coal-fired utility FGD systems are shown in Figure 1.[3]

In the late 1970's the projected annual rate of application of regenerable FGD systems is expected to exceed that for the non-regenerable FGD systems. These systems produce a variety of sulfur-containing by-products which represent alternatives to the non-regenerable sludge, including elemental sulfur, sulfuric acid, gypsum, sodium sulfate, ammonium sulfate, and liquid SO_2.However, based on current emphasis, technology availability, and lead time considerations, most of the FGD systems installed by 1980 are expected to be lime/limestone.[2] Other applications of lime/limestone scrubbing (e.g., oil-fired utility boilers, coal-fired industrial boilers) could make the 90,000 Mw projected for control by these processes a realistic figure.

3.3 Quantification of the Problem and Comparison with Analogous Environmental Problems

One of the major problems inherent in any FGD system is the necessity to dispose of or utilize large quantities of a sulfur product. Lime/limestone (and double alkali) scrubbing systems generate throwaway sludge products with little commercial value projected at the present time.



Notes:

Curves include new and existing plants requiring controls to achieve either primary standards or new source performance standards.

[a] Based on pessimistic projections for new low sulfur coal supplies and minimal redistribution of existing supplies.

[b] Based on optimistic projections for low sulfur coal supplies and maximum redistribution of existing supplies.

Figure 1. CUMULATIVE NEED: FGD FOR COAL FIRED POWER PLANTS

A power plant SO_2 scrubbing system can be designed with the alternatives of collecting flyash simultaneously with the flue gas scrubbing operation or of collecting flyash upstream of the scrubbing operation by precipitators and/or mechanical collectors. Additionally, the ash may be disposed of separately or with the scrubber sludge. As yet, no consistent approach has been taken by the utility industry. For coal-fired installations where efficient particulate removal does not take place upstream of the wet lime/limestone absorber, scrubber sludges can contain large quantities of coal ash.

The amount of sludge generated by a given plant is a function of the sulfur and ash content of the coal, the coal usage, the load factor (on-stream hours per year), the mole ratio of additive to SO_2, the SO_2 removal efficiency of the scrubbing system, the composition of the sludge (e.g., sulfite/sulfate ratio), and the moisture content of the sludge. Table 1 shows typical quantities of ash and sludge produced by a plant burning the national average (3 percent S, 12 percent ash) coal projected for 1980, and using a lime/limestone scrubbing system. Quantities for combined and separate disposal of sludge and ash are given to show the effects of these options.

Assuming the projected 90,000 Mw of FGD control is accomplished entirely by lime/limestone installations and using the national average annual sludge production rate per 1000 Mw of controlled generating capacity, the amount of wet sludge and ash (limestone sludge, combined disposal, 50 percent moisture) that will have to be disposed of annually by 1980 could be as high as 118,000,000 metric tons/year (130,000,000 tons/year). (It is unlikely that all coal-fired utility FGD installations will be lime/limestone systems. However, the majority are expected to be and other applications, e.g., oil-fired utility boilers, coal-fired industrial boilers, could make the projected sludge production figure quite realistic). Depending on the viability and commercial availability of alternate clean fuel technologies, sludge production rates could substantially increase in the post-1980 period.

Although the quantities of sludge produced by a large power plant are considerable, they should be put in perspective by the comparisons discussed below. Table 2 shows the annual land and solid waste impact of a 1000 Mw coal-fired electric energy system equipped with flue gas desulfurization (FGD) for SO_x and particulate removal.[4] The coal mining operations appear to have the greatest impact in terms

TABLE 1. TYPICAL ANNUAL PRODUCTION OF ASH AND SLUDGE BY A 1000 MW COAL-FIRED GENERATING STATION CONTROLLED WITH LIME/LIMESTONE FLUE GAS DESULFURIZATION SYSTEM (Quantities In Short Tons)[a]

Coal Ash, dry	338,000
Coal Ash, wet (80% solids)	422,000
Limestone Sludge, dry[b]	
$CaSO_3 \cdot 1/2H_2O$	260,000
$CaSO_4 \cdot 2H_2O$	29,000
$CaCO_3$ (unreacted)	92,400
TOTAL	381,400
Limestone Sludge, wet (50% solids)	762,800
Limestone Sludge + Ash, wet (separate disposal)	1,184,800
Limestone Sludge + Ash, wet (combined disposal, 50% solids)	1,438,800
Lime Sludge, dry[b]	
$CaSO_3 \cdot 1/2H_2O$	260,000
$CaSO_4 \cdot 2H_2O$	29,000
CaO (unreacted)	22,200
TOTAL	311,200
Lime Sludge, wet (50% solids)	622,400
Lime Sludge + Ash, wet (separate disposal)	1,044,400
Lime Sludge + Ash, wet (combined disposal, 50% solids)	1,298,400

Assumptions:

Coal:	3.0%S; 12% ash
Plant:	$6400 \frac{hr}{yr}$, $0.88 \frac{lb\ coal}{kw\text{-}hr}$
Scrubber:	85% SO_2 removal; 1.0 CaO/SO_2 mole ratio; 1.2 $CaCO_3/SO_2$ mole ratio

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[a] 1 short ton = 0.907 metric ton.

[b] Sulfite/sulfate ratio based on performance of Chemico scrubbing unit at Mitsui Aluminum Company, Japan.

TABLE 2. COMPARATIVE ANNUAL LAND AND SOLID WASTE IMPACT OF 1,000 MW ELECTRIC ENERGY SYSTEM (0.75 LOAD FACTOR)

(Low Levels of Environmental Controls Except for Installation of a Limestone FGD System for SO_x and Particulate Removal)

	Mining (Coal)[4]		Processing[4]	Transport[4]	Conversion[4] (plant site)	Limestone FGD System[a], Untreated Ponded Sludge	Transmission[4]	Totals	
	Deep	Surface						Deep	Surface
Land Affected, acres[b]	9,120	14,010	161	2,213	350	367 (30 ft. depth)	17,188	29,399	34,289
Solid Waste Produced, short tons[c]	97,141 (wet, 97% solids) (101,346 with acid drainage sludge)	2,762,000 (wet, 98% solids) (2,762,328 with acid drainage sludge)	454,092 (wet, 99% solids)	0	0	1,440,000 (wet, 50% solids)	0	1,991,233	4,656,092
Environmental Impact	1) potential land degradation due to subsidence; 2)acid mine drainage water pollution problems	1) mined land made barren precluding wildlife habitat, recreation and most other uses; 2)acid mine drainage water pollution problems	1) culm piles; 2) water pollution: a) acid drainage; b)siltation; 3)air pollution: a)Discharges SO_2, CO &H_2S; b)potential spontaneous combustion	use of land for railroad beds	use of land for power plant site	1) potential groundwater pollution problems; 2)land potentially made useless if sludge not treated or permanently dewatered	use of land for transmission line right of way	N/A	N/A
Typical Technique(s) Available to Minimize Impact	1)no well developed cost-effective technology to control subsidence; 2)neutralization of mine drainage with lime	1)intensive land reclamation can restore most strip-mined land;2) neutralization of mine drainage with lime	compacting in holes, mines, quarries, etc.	N/A	N/A	1)although reclamation is feasible, no well developed, cost-effective technology has been demonstrated; 2)sound pond management, use of impermeable pond liner and operation of FGD system in closed-loop mode can minimize water pollution. (As an alternative to ponding, chemical fixation with landfill appears to have potential for solving both water pollution and land reclamation problems.)	N/A	N/A	N/A

[a] See Table 1 for assumptions (also includes ash)

[b] Land affected is expressed as a time average of the amount of land in use over 30 years. Fixed land is taken at its full amount; average variable use (waste storage) is 15 times the annual incremental damage.

[c] 1 short ton = 0.907 metric ton.

of land use and environmental effects. Although the right-of-way required for transmission lines actually consumes more land than coal mining, this land is still available for some other uses and, aside from aesthetics, the environmental effects are minimal.

The area required for the site of a plant equipped with a lime/limestone FGD system and using ponding for combined sludge and ash disposal would be just over 2 times as much total area as a plant site without the SO_x and particulate control system. For comparison, this same plant site area would be about 1.5 times the total area of a plant with particulate control only and ash disposal by ponding.

Table 2 also shows that large quantities of wastes are involved in coal mining and processing operations. It can be seen that the FGD system will produce about 3 times as much waste as deep mining, but only about half that produced by strip mining.

Table 3 presents a semi-quantitative comparison of major U.S. solid wastes on a dry basis. In addition to quantities of waste, disposal methods and potential environmental problems are shown. Quantities are not directly comparable in every case since they are based on many different sources and time periods.

The quantities of dry sludge (excluding ash) projected to be produced in 1980 by plants using lime/limestone FGD systems are about 40 percent of projected 1980 production rates of coal ash from all power plants. They are about 34 percent of recent production of ore wastes. However, the quantities are greater than those for municipal sewage sludge, phosphate rock slime, gypsum from fertilizer manufacture, or acid mine drainage sludge.

As shown in Table 3, ponding and landfilling provide the major mechanisms of disposal of most waste products. In terms of environmental effects, these disposal mechanisms have many points of similarity for the various industries. In some cases, land use for waste disposal has destroyed wildlife habitat and is aesthetically objectionable. In addition, all wastes have the potential for varying degrees of surface and groundwater pollution depending on their chemical compositions and solubilities, and the location, design, and operation of the disposal site. To reclaim the disposal site, most of the stable wastes require only a cover material to support growth of vegetation and to prevent eventual erosion of the wastes by run-off water. However, some wastes (e.g., phosphate rock slime, sewage sludge) are resistant to dewatering. In these cases, the disposal sites could become only

TABLE 3. COMPARISON OF MAJOR SOLID WASTE DISPOSAL PROBLEMS

Waste Material	Quantity Disposed Annually In Referenced Year, metric tons, dry	Method of Disposal	Land Use or Reclamation Considerations
Municipal and Industrial Refuse [5]	270,000,000[a] (1973)	Landfilling, incineration	Cover material needed to support vegetation.
Culm Piles[6]	>100,000,000 [b] (1969)	Surface piles, landfilling	Cover material required for plant growth. Provision for collection of drainage.
Mineral Ore Wastes [c]	89,000,000 [7] (1970)	Ponding, surface piles, landfilling	Needs cover material.
Coal Ash (including coal ash from lime/limestone scrubbing installations)	75,500,000[d] (1980)	Ponding, landfilling	Needs cover material.
Lime/limestone Scrubber Sludge (excluding coal ash)	32,000,000 [e] (1980)	Ponding, landfilling	Untreated sludge difficult to dewater.
Taconite Tailings [8]	55,000,000 (1971)	Ponding; lake dumping (Reserve Mining Company only)	Fertilization, mulching, etc. required for reclamation of ponds.
Gypsum from Fertilizer Manufacture [9]	25,000,000 [f] (1973)	Ponding, surface piles	Needs cover material to support vegetation and make aesthetically acceptable.

TABLE 3. (Continued) COMPARISON OF MAJOR SOLID WASTE DISPOSAL PROBLEMS

Waste Material	Quantity Disposed Annually In Referenced Year metric tons, dry	Method of Disposal	Land Use or Reclamation Considerations
Municipal Sewage Sludge[10]	11,000,000 (1980)	Ponding, landfilling	Hard to dewater. Difficult to develop.
Phosphate Rock Slime[11]	1,800,000 [f] (1967)	Ponding	Hard to dewater (settles to only 30% solids after years). Not established whether dried solids will support vegetative growth.
Acid Mine Drainage Sludge[12]	410,000 [g]	Ponding	Hard to dewater.

[a] Excludes agriculture & mining wastes

[b] Bituminous coal only

[c] Rock wastes from metal ores only; no processing wastes included

[d] 12% Ash, 6400 hrs/yr, 245,000 Mw installed coal fired generating capacity (1980), 0.88 lb coal/Kwhr

[e] 3% S, 12% Ash, 6400 hrs/yr, 85% SO_2 Removal, 0.88 lb coal/Kwhr, 90,000 Mw controlled generating capacity, 1.2 $CaCO_3/SO_2$ (inlet) mole ratio, 10% oxidation

[f] 80% disposed of in Florida.

[g] Most acid mine drainage comes from abandoned mines and these are not treated.

a temporary storage site. Although land reclamation is feasible, no well-developed technology, other than fixation, appears to be established. However, with proper site selection and design (including a permanent, impermeable liner) and sound operating practices, surface water and groundwater pollution can be avoided.

3.4 Nature of the Material

Scrubber sludge is normally a moist, grey material containing varying amounts of flyash from the combustion process. (If no flyash were present, the material would be white.) The physical behavior of the sludge is primarily dependent on the percentage of retained moisture. However, the degree to which a sludge can be dewatered is dependent on the relative quantities of the major solid constituents present, i.e., calcium sulfite, calcium sulfate, calcium carbonate (and/or calcium hydroxide), and flyash. The moisture-retaining tendency has been attributed to the thin, platelet-like crystal structure of calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$). The result of this moisture is thixotropic behavior, with the sludge exhibiting little or no compressive strength. This behavior can be substantially modified by several techniques, which are discussed in Section 5.1.

Table 4 compares a sludge with high calcium sulfite content (typical of high-sulfur Eastern coal-fired plants) to a sludge with high calcium sulfate content (typical of low-sulfur Western coal-fired plants).

TABLE 4. COMPARISON OF TYPICAL SLUDGE DEWATERING PROPERTIES[13,14]

Sludge Type	Approximate Degree of Dewatering, percent solids		Approximate Percent Solids for Optimum Compaction
	Settling	Filtration	
High $CaSO_3 \cdot 1/2H_2O$ (low flyash)	30-35	50	80
High $CaSO_3 \cdot 1/2H_2O$ (high flyash)	35-40	55-60	80
High $CaSO_4 \cdot 2H_2O$ (low flyash)	60-65	80	90

It should be noted that the presence of significant amounts of flyash will slightly alter the dewatering characteristics by increasing the solids content of sulfite sludges but slightly decreasing the solids content of sulfate sludges (the percent solids for optimum compaction of flyash is about 80). Another significant point to note is the wide gap between the percent solids for filtered calcium sulfite sludge and the percent solids required for optimum compaction of that material. This is an important consideration in examining disposal options. A final point is that since sludges vary from plant to plant, the physical behavior will vary between the figures shown in Table 4.

The major constituents of scrubber sludge range from very slightly water soluble (e.g., calcium carbonate, calcium sulfate) to water insoluble (flyash). Although some of the constituents are soluble in acid, the presence of alkaline materials makes their dissolution unlikely. The sludge liquors contain dissolved species in concentrations which vary with individual solubilities and the rate at which the species enter the scrubbing system. The prevalent ions include calcium, sulfate, chloride, and magnesium. The liquors and solids also contain trace elements, primarily from the flyash and coal. From an environmental standpoint, the constituents of the sludge liquor are the most significant, since they represent the potential ground water pollution problem for untreated sludge disposal on land. Based on data from sludge liquors analyzed thus far,[13,14] the following constituents are of concern:

(1) Mercury
(2) Selenium
(3) Boron
(4) Chloride
(5) Sulfate
(6) Total Dissolved Solids (primarily calcium, chloride, sulfate)

All of these constituents have appeared substantially in excess of water quality criteria. These results strongly indicate that environmentally sound scrubber sludge disposal techniques (such as chemical fixation or ponds lined with impermeable materials) need to be employed.

In summary, the nature of the sludge indicates problems which must be addressed by the lime/limestone process user. Various approaches have been or are being investigated, including commercial utilization of the sludge and a variety of sludge disposal techniques.

4.0 CURRENT APPROACHES TO DISPOSING OF OR UTILIZING SCRUBBER SLUDGE MATERIALS

4.1 Commercial Utilization

Investigations into the potential commercial utilization of power plant desulfurization sludges have been made by numerous government and private organizations. These organizations include Federal agencies; research centers; universities; commercial research, processing and sales corporations; national trade associations; and private researchers. The results of their efforts have been disseminated through symposia, technical reports, newspapers and periodicals. A review of these references indicates that the general consensus is that, although some commercial usage is feasible from a technical and economic standpoint, the potential outlet is so small that the vast majority of the sludges will not be marketed.

Attempts have been made to develop technology to apply sludges to the existing ash product market or to develop new applications in which the sludges might be used. Such developments and investigations have been reported by research centers including the Coal Research Bureau - West Virginia University, Combustion Engineering, IU Conversion Systems, Inc. and Michigan Institute of Technology. These developments include mineral wool, bricks, sintered concrete products, soil amendment, sulfur recovery, gypsum, mineral recovery, road base materials, parking lot materials, artificial aggregate, lightweight aggregate, and aerated concrete. It was eventually recognized that despite the fact there were many potential flyash products with quality equal to or superior to other existing materials, the use of flyash was limited; it was also recognized that the situation would be even worse for sludge. Major inhibitions to the use of sludge include highly variable chemical and physical properties, high transportation costs, requirement for dewatering for many applications, and inability to economically compete with other materials.

This is in contrast with the trend in Japan, which since 1972 has been toward the conversion of scrubber sludge to gypsum. All of the gypsum has been used so far for wallboard production and as a retarder of cement setting. It should be noted that the presence of flyash in appreciable quantities reduces the market value of the wallboard gypsum in Japan[15] but, since most Japanese boilers are oil-fired, this does not present a major problem. This could present a marketing problem for applying this approach to the coal-fired systems in the U.S. unless most of the flyash is removed ahead of the scrubber.

Although the supply of gypsum in Japan is expected to exceed the demand in the next few years, and despite the fact that land there is at a premium, the trend toward byproduction of gypsum continues because gypsum is considered more acceptable for disposal.[15] This is due primarily to the fact that gypsum is much more easily dewatered than sludge containing large quantities of calcium sulfite. Consequently, the volume of sludge for disposal is substantially reduced. Conversion to gypsum also eliminates any chemical oxygen demand which the calcium sulfite might present.

Since gypsum is a relatively plentiful commodity in the United States (although much of it is imported), conversion of scrubber sludge to gypsum is not expected to be a major utilization activity. However, it does present a potential alternative to other disposal schemes.

From the above discussion, it is concluded that for the immediate future, disposal of scrubber sludges will be the major alternative selected in the United States. The discussion below summarizes current utility programs for sludge disposal.

4.2 Present and Planned Utility Industry Disposal Programs

The major options for sludge disposal are ponding and landfill. Table 5 summarizes dewatering techniques and ultimate disposal modes for fifteen lime and limestone FGD systems at utility sites. It can be observed that utilities are selecting both ponding and landfill as the disposal mode. For those sites selecting the landfill mode, dewatering techniques (such as filtration or centrifugation) and/or sludge fixation processes have been or will be used to attempt to produce an acceptable landfill material.

The wide variety of approaches indicated may be based on factors such as: non-uniformity of local regulations, disposal site location and ownership, disposal site proximity to ground or surface waters, soil permeability, variations in sludge chemical and physical properties, and variations in scrubber processes and types of ash collection and disposal.

Detailed examples of some of the utility sludge disposal programs are described below:

Commonwealth Edison (Will County) - Treated sludge material will be stored in clay-lined basins with groundwater wells. The material will cure for approximately one month and will be

TABLE 5. SLUDGE TREATMENT/DISPOSAL TECHNIQUES FOR SELECTED UTILITY LIME/LIMESTONE FGD SYSTEMS

(X = Current; P = Possible Additions)

Facility (Operating Status)	Sorbent	Fuel	Scale	Dewatering Technique					Final Disposition	
				Clarifier	Filter	Centrifuge	Dryer	Pond	Ponding	Landfill
TVA-Shawnee (Current) EPA Test Facility	Limestone & lime	Eastern coal	Prototype (Three 10 Mw Units)	X	X	X			X (unlined)	
City of Key West-Stock Island (Current)	Limestone (coral marl)	Residual oil	Full					X		X (unfixed)
Commonwealth Edison Co.-Will County (Current)	Limestone	Eastern coal	Full	X	P		P	X (clay-lined well points)		X (fixed)
Southern California Edison-Mohave Lime: Current Limestone: Oct. 1974	Limestone & lime	Western coal	Full	X	X				X (fixed)	
Kansas City Power & Light-Hawthorn (Current)	Limestone - boiler injected (Unit 3) and "tail-end" (Unit 4)	Coal (possible E&W blend)	Full	X				X (well points)	X (unlined)	
Kansas Power & Light-Lawrence (Current)	Boiler injected limestone	Eastern coal	Full					X	X (unlined)	
Louisville Gas & Electric-Paddy's Run (Current)	Carbide sludge ($Ca(OH)_2$)	Eastern coal	Full	X	X					X (unfixed)

TABLE 5. (Continued) SLUDGE TREATMENT/DISPOSAL TECHNIQUES FOR SELECTED UTILITY LIME/LIMESTONE FGD SYSTEMS

(X = Current; P = Possible Additions)

Facility (Operating Status)	Sorbent	Fuel	Scale	Dewatering Technique					Final Disposition	
				Clarifier	Filter	Centrifuge	Dryer	Pond	Ponding	Landfill
Northern States Power-Black Dog (Current)	Limestone	Western coal	Prototype (3-5 Mw)	X					X (unlined)	
Kansas City Power & Light-LaCygne (Current)	Limestone	Eastern coal	Full						X (unlined)	
Arizona Public Service-Cholla (Current)	Limestone	Western coal	Full						X (solar evap) (unlined)	
Duquesne Light-Phillips (Current)	Lime	Eastern coal	Full	X				X (curing) (unlined)		X (fixed)
Detroit Edison-St. Clair (Jan. 1975)	Limestone	Eastern coal	Full					X		X (unfixed)
TVA-Widows Creek (1976)	Limestone	Eastern coal	Full					X	X (unlined)	
Pennsylvania Power- Bruce Mansfield (1975/1976)	Lime	Eastern coal	Full	X						X (fixed)
Northern States Power-**Sherburne** (1976/1977)	Limestone-Flyash	Western coal	Full	X					X (clay lined)	

inspected by local authorities to obtain permission for off-site disposal. Activities to determine the technical quality of the fixed material and attendant costs are still underway.

Kansas City Power & Light (Hawthorn) - Fourteen wells are located around the unlined on-site pond and are sampled periodically. No definite data are available but it is believed that results to date are inconclusive because the groundwater in the general area may be heavily contaminated by leachates from on-site flyash ponds.

Duquesne Light Company (Phillips) - After curing for about 30 days in clay-lined basins, sludge treated with Dravo's "Calcilox" is being dredged out and hauled to a disposal demonstration site about one mile away. The site includes two ponds lined with Hypalon. Each pond has underdrainage and overdrainage piping provisions to collect water for testing. These demonstration tests are still underway.

Southern California Edison (Mohave) - Two commercial sludge fixation processes are currently being evaluated. The Dravo process is being demonstrated through production of a landfill (soil-like) material; the IUCS process is being demonstrated through production of a synthetic aggregate. Tests are being conducted to determine the environmental acceptability of these materials.

Through activities of the type described above, utilities, FGD vendors, and sludge handling technology vendors can be expected to identify environmental problems and solutions, and to optimize costs of sludge disposal, as necessary for their specific applications. However, it is felt that more information and data are necessary to assure more general application of sludge disposal technology and to further minimize environmental effects, at reasonable cost. In an attempt to fulfill those needs, EPA has initiated several programs, which are discussed below.

5.0 CURRENT EPA R&D PROGRAMS

5.1 Aerospace Study

The most broadly-based EPA program relating to scrubber sludges is the National Environmental Research Center-Research Triangle Park, N.C. (NERC-RTP) contract with The Aerospace Corporation (El Segundo, California) entitled "Study of Disposal of By-Products From Non-Regenerable Flue Gas Desulfurization Systems." This study was initiated during late 1972 and has the following major elements:

(1) An inventory of sludge constituents in both the solid and liquid phases. Sludges produced from the following sorbent/fuel combinations are being studied: limestone/Eastern and Western coals, lime/Eastern coal, and double alkali/Eastern and Western coal.

(2) An evaluation of the potential water pollution and solid waste problems including consideration of existing or proposed water effluent, water quality and solid waste standards or guidelines.

(3) An evaluation of treatment/disposal techniques with emphasis on ponding and treated and untreated landfill. In particular, sludges treated by two or more commercially offered processes will be evaluated in the laboratory for mechanical properties, permeability, leachability, etc.

(4) A recommendation of the best available technology for sludge treatment/disposal based on the elements delineated above.

(5) Support of an EPA field study of FGD sludge disposal at TVA's Shawnee Steam Plant, which will include test planning, program coordination, analyses of liquid and solid samples, and reports.

Initial results of the Aerospace contract were reported in May 1974.[16] A second report should be issued in mid-1975. The final report of the effort is expected to be released in late 1976. Sections 5.1.1 and 5.1.2 summarize recent information generated under this contract; this information was reported in detail in two previous papers.[13,14]

5.1.1. Sludge Chemical and Physical Characterization

In the Aerospace Corporation study, sludge samples have been analyzed from three scrubbers involving lime/Eastern coal, limestone/Eastern coal and limestone/Western coal. (Samples from two additional scrubbers were analyzed under a NERC-Corvallis study. Results of these analyses have also been assessed as part of the NERC-RTP study.) Chemical characterizations of the sludge liquors were performed to identify the concentrations of nine trace metals of interest and seven major soluble species, as well as the pH and total dissolved solids (TDS) for each of the samples collected. (Input materials such as coal, flyash and make-up water were also characterized to identify sources of constituents found in the sludges.) By comparing the analytical data with the EPA Proposed Public Water Supply Intake Criteria (October 1973),[17] a preliminary assessment was made with regard to any potential environmental problem that might be posed if these sludge liquors entered water supplies.

In assessing the potential impact of trace metals, it was found that in each of the sludge liquors at least one of the following trace metals exceeded the EPA proposed criteria: arsenic, cadmium, chromium, lead, mercury, and selenium. Except for mercury and selenium, these trace metals exceeded the criteria by not more than a factor of 5. Mercury and selenium exceeded the criteria in each of the sludges analyzed by more than an order of magnitude. Comparing the concentrations of the major soluble species with the criteria, it was found that particular excesses exist for chloride, sulfate and TDS for each of the samples analyzed. To date, only one sample has been analyzed for boron, which was also found to be in excess. It should be noted that most of the constituents of concern originate in the coal, indicating that FGD processes provide a multi-pollutant control capability.

The assessment indicated that in all of the power plant sludge liquors analyzed, water quality criteria are appreciably exceeded for mercury, selenium, boron, chloride, sulfate and TDS (See Section 3.4). Attenuation of chemical species by soil is widely accepted in many land disposal practices; however, attenuation of three of the species discussed above, namely, selenium, boron and chloride, is known to be ineffective. Whether the concentrations of the other constituents are acceptable or not, the concentrations of these three species strongly indicate that environmentally sound techniques such as lined ponds or chemical fixation are needed for scrubber sludge disposal.

Detailed physical characterization of various samples have also been performed under the Aerospace Corporation study to determine properties such as: ease of dewatering/settling, bulk density, viscosity, load bearing strength and permeability. Results of the characterization have verified the water retentive nature of calcium sulfite and have quantified the effect of moisture on sludge physical properties. For example, at 65 percent solids content, sludges will support personnel, and at solids content greater than 70 percent, sludges will support heavy equipment. However, the cost of dewatering the sludge and maintaining the disposal site at the necessary degree of dryness is strongly dependent on the raw sludge properties, and may or may not compare favorably with the cost of an alternative disposal technique such as chemical fixation.

5.1.2. Current Disposal Techniques

Ponding - Available information indicates that water pollution problems can be prevented by proper pond engineering, installation of an impervious pond liner, and by operating the FGD system in a closed-loop mode. Pond liners may consist of flexible materials such as polyethylene, polyvinyl chloride, du Pont Hypalon films, or non-flexible materials such as asphalt concrete or clay. Costs of ponding are primarily dependent on construction costs and the type of liner employed, with a minor dependency on the cost of land. Estimated costs for ponding of sludge range from about $2.50 to $4.50 per ton of wet (50% solids) sludge, exclusive of possible pond reclamation costs.

Ponding of scrubber sludge containing considerable amounts of calcium sulfite has the disadvantage--in areas of the country where precipitation exceeds evaporation (this is the case in most of the Eastern U.S.)--of excessive moisture being retained in the sludge (see Section 3.4). Under these conditions the sludge has little compressive strength, and presents a land reclamation problem which can be avoided by chemical treatment (fixation). Sludge consisting mostly of calcium sulfate (gypsum) may not present this problem, but this has not yet been demonstrated. Even if land reclamation difficulties are avoided, eventual deterioration of pond linings would still be of concern. Available data indicate that chemical treatment could avoid the need for a pond lining.

Landfill - The problems in landfilling untreated scrubber sludge are identical to those of ponding the material, except that additional dewatering is normally necessary. As discussed previously, this presents the most difficulty with sludges containing considerable calcium sulfite. Commercial processes for chemical treatment (fixation) of scrubber sludge are currently offered by at least three companies--Chemfix (Division of Environmental Sciences, Inc.), Dravo Corporation, and IU Conversion Systems, Inc. (IUCS). Although distinctly different chemicals and operations are employed, all three processes are designed to produce a material with sufficient compressive strength to be suitable for landfill and to chemically and/or physically bind up the soluble constituents of the sludges.

Costs of sludge chemcial treatment (fixation) processes are still developing, and depend to a great extent on the local plant conditions, e.g., land availability. Estimates from various sources indicate chemical fixation costs of from $2 to $9 per (short) ton of sludge (wet, 50 percent solids). All relevant factors pertaining to the cost estimates are not available, but based on recent vendor contacts, a total cost for treated scrubber sludge disposal of about $5/ton appears reasonable. (In a typical power plant application, $5/ton would be equivalent to 1.2 mills/Kwhr.) These costs are for disposal in natural soil disposal sites, which means sludge fixation costs are more than the costs of disposal in a lined pond. However, the potential for future environmental difficulties is substantially reduced.

As indicated in Section 3.4, scrubber sludge consisting mostly of gypsum is much more easily dewatered than other scrubber sludges. If most of the solubles could also be removed by techniques such as cake washing, this material might be suitable for direct disposal on land.

The FGD processes applied to utilities using low-sulfur Western coal normally produce high gypsum sludge. Technology also exists for conversion of high calcium sulfite sludges to gypsum sludges. If landfilling of untreated gypsum sludge proves feasible, this would provide a direct competitor to chemical fixation.

5.2 Shawnee Field Study

5.2.1 Overview

A field study of sludge disposal has been initiated by NERC-RTP at the Tennessee Valley Authority (TVA) Shawnee Steam Plant near Paducah, Kentucky. The purpose of the study is to evaluate current sludge disposal technology regarding the ponding of raw sludges and simulated landfilling using chemical-treated sludges. The study, which began in September 1974, will last approximately 18 months.

The disposal test site contains clay-like soils such that all disposal areas will simulate clay lined ponds or basins. Five different disposal ponds, each approximately 405 sq m (0.1 acre) in size, will be filled to a depth of about 0.9 m (3 ft). One will contain untreated filter cake from the venturi-spray tower (lime) scrubber and one will contain untreated clarifier underflow from the mobile bed (limestone) scrubber. Each of the three other ponds will be filled by sludge fixation process contractors as follows:

(1) Chemfix-treated limestone clarifier underflow, averaging about 40 percent solids which contain about 45 percent flyash (dry basis).

(2) IUCS, Inc.-treated lime filter cake averaging about 50 percent solids which contain 45 percent flyash (dry basis).

(3) Dravo-treated limestone filter cake averaging about 55 percent solids which contain 45 percent flyash (dry basis).

All fixation will be performed on-site during the period November - December 1974. No additional materials, such as flyash or soil will be used for further dewatering of the sludge. Technical and economic data attendant to each of the pond sludge operations will be collected to determine an estimate of fixation costs for disposal of a similar material at a full-scale plant.

Each pond will have a leachate well and ground water wells, all of which will be sampled periodically. Soil cores from the pond bottoms will be taken prior to filling and periodically throughout the program; fixed sludge cores will also be taken periodically.

In addition, sludge samples from the scrubber system discharge (clarifier underflow or filter cake) will be taken as well as periodic samples of disposal pond surface liquors. Selected analyses of all samples will be conducted by TVA and Aerospace to determine the following: 1) the nature of the bottom soil of each pond; 2) the quality of the water from all wells; 3) the seepage through the bottom of all ponds; 4) the interaction between the sludges and the bottom soil of each pond; 5) the quality of the chemically conditioned sludges as to strength, permeability, and leaching effects.

All construction, maintenance, sampling and selected testing will be performed by the TVA. The Aerospace Corporation is responsible for developing and maintaining the test plan, coordinating the program, performing selected tests, analyzing the test data and writing the final report. Bechtel Corporation will coordinate the scrubber test program with the disposal study as necessary. A status report will be released in mid-1975 and the final report will be issued in late 1976.

5.2.2 Current Status

The first untreated sludge pond was filled in late September-early October 1974. Designated Pond "A", this pond was filled with filter cake from the venturi-spray tower lime scrubbing system. Figure 2 shows the filter cake discharge; the filter cake drops to a horizontal conveyor, then is transferred to an inclined portable conveyor (Figure 3), which deposits the filter cake into a cement truck. During filling of the truck, the cement mixer is rotated, keeping the sludge in a fluid state.

Figure 4 shows Pond "A" prior to filling. Figure 5 is a close-up of the leachate well and access platform. Figure 6 shows the cement truck in position for discharge of the sludge. Figure 7 is a close-up of the sludge in Pond "A" when the pond was approximately half full. In the foreground the surface of the sludge has dried and has begun to crack.

After Pond "A" was filled, the filling of the second untreated sludge pond was initiated. Designated Pond "D", this pond was filled during October 1974 with clarifier underflow from the mobile bed limestone scrubbing system. In early November, the

Figure 2. Discharge of Sludge Filter Cake

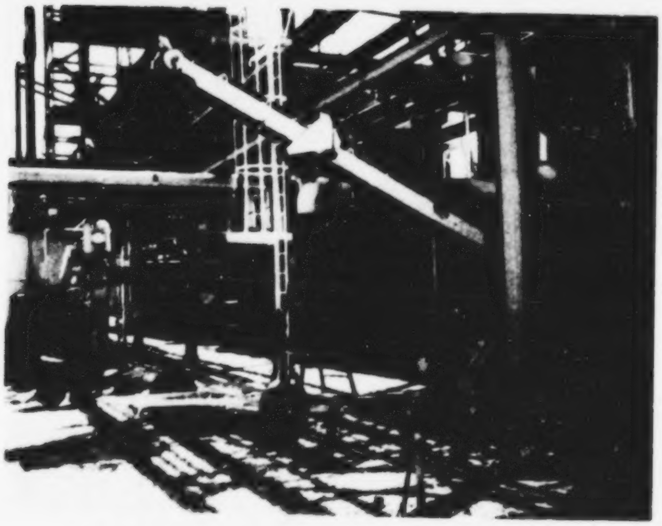

Figure 3. Portable Sludge Conveyor

Figure 4. Pond "A" Prior to Filling

Figure 5. Pond "A" Leachate Well & Access Platform

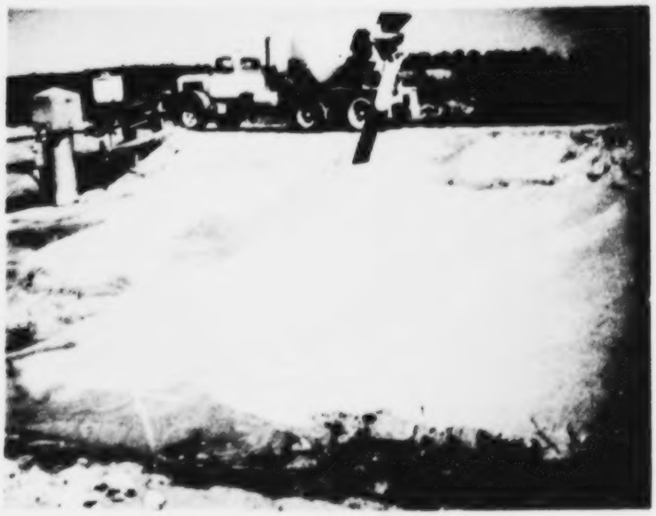

Figure 6. Cement Truck in Position to Discharge Sludge in Pond "A"

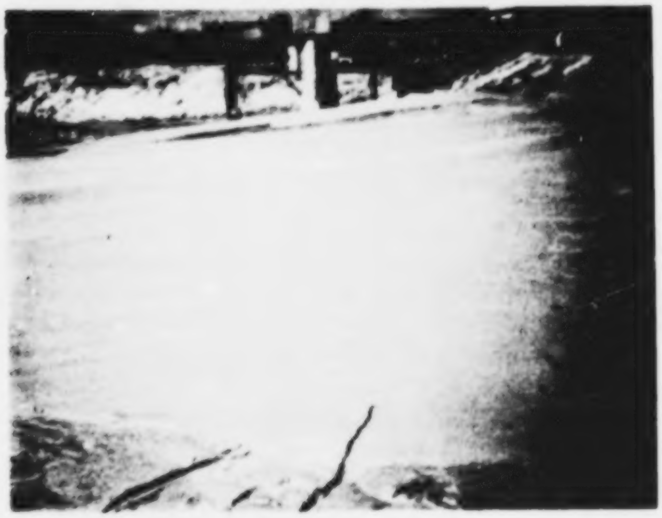

Figure 7. Pond "A" Half-Filled with Sludge

sludge from this pond will be treated by the Chemfix process and placed in an adjacent pond, designated Pond "E". Pond "D" will be refilled with untreated limestone sludge, according to current plans, beginning in mid-December. The remaining ponds (Pond "B" and Pond "C") are expected to be filled with treated sludge during the period early November - early December.

5.3 Corps of Engineers Fixation Studies

5.3.1 Overview

In mid-1974, NERC-Cincinnati initiated an interagency agreement with the U.S. Army Corps of Engineers' Waterways Experiment Station in Vicksburg, Mississippi. Under this agreement, the leachability and durability of raw and chemically fixed hazardous industrial wastes (Type "A" sludges) and FGD scrubber sludges (Type "B" sludges) will be studied. Five Type "A" sludges and up to six Type "B" sludges will be obtained for the study. In addition, five fixation processors will be selected to treat each of the two categories of sludges (not necessarily the same five processors for each sludge category).

The program will be conducted in three phases:

(a) Phase I will consist of sludge characterization and analysis, preliminary leaching tests, and the design of the testing program for Phase II.

(b) Phase II will include laboratory studies of leachability, permeability, durability, and stability tests. The leachability tests will consist of column studies designed to simulate field conditions associated with land disposal.

(c) Phase III will be a field study during which selected sludges will be disposited directly on land surface plots (simulated landfill).

Formal progress reports on the effort are expected to be issued as follows:

(a) Laboratory Report on Leachability and Durability Studies (Phases II and III) - mid-1975.

(b) Interim Report on Field Study (Phase III) - mid-1976.

(c) Final Report on Field Study - mid-1977.

The leachability and durability studies are expected to supplement and enhance the efforts being conducted under the Aerospace study (Section 5.1). The field studies should supplement the information generated in the Shawnee field study (Section 5.2). The EPA project officer for this study is Mr. Robert Landreth.

5.3.2 Current Status

The scrubber sludges obtained by the Corps of Engineers so far in this study include the following:

Eastern (high-sulfur) coal - lime
- limestone
- double alkali

Western (low-sulfur) coal - limestone
- double alkali

As of September 30, 1974, samples of most of the sludges had been sent to the appropriate fixation processors. A total of seven processors were selected for this study. Three of the seven will be treating both the (Type "A") industrial sludges and the (Type "B") scrubber sludges.

Preliminary qualitative and quantitative analyses have been conducted of the scrubber sludges and the industrial sludges. In addition, two sets of elutriate (batch-wise leachate) samples have been obtained and analyzed. The first set were obtained by contacting the sludges with deionized water, the second set by contacting the sludges with deionized water adjusted to pH 4.0 with $HC\ell$. Since these data have not been completely analyzed, they are not reported here.

The leachate column studies were expected to be underway in late October 1974.

5.4 Dugway Proving Ground Study

In January 1974, NERC-Cincinnati initiated an interagency agreement with the U.S. Army Materiel Command's Dugway Proving Ground, Dugway, Utah, to determine the extent to which heavy metals and other chemical constituents from five industrial wastes could migrate through the soil in land disposal sites. In mid-1974, this study was expanded to include eight additional industrial wastes and three untreated FGD scrubber sludges.

The program will be conducted in three phases:

(a) Phase I will consist of physical and chemical characterization of the sludges and preliminary screening tests with a variety of U.S. soils.

(b) Phase II will consist of leachate studies in columns with the sludges applied to two selected (best and worst) soils. Long term permeability tests with selected clays are also planned for the FGD scrubber sludges.

(c) Phase III will consist of data interpretation of the Phase II tests to identify soil attenuation mechanisms and to develop empirical "attenuation coefficients" for specific chemical substances.

The Phase I results will supplement the Aerospace and Corps of Engineers' efforts. The Phase II results are expected to assist considerably in interpretation of the results of the Shawnee field study, particularly the permeability tests with clays.

Results of the Phase I screening tests with scrubber sludges are expected to be reported by mid-1975. Preliminary results of the column studies are expected to be reported in late 1975; the final results are expected to be reported in late 1976. As of October 22, 1974 Phase I with the scrubber sludges was almost ready to be initiated. The EPA project officer for this study is Dr. Michael Roulier.

5.5 Full-Scale Sludge Demonstration Program

NERC-Cincinnati is currently considering a full-scale sludge disposal demonstration program with a utility which uses high sulfur coal. This program would serve to supplement the Shawnee field demonstration. The program, if it is undertaken, would include laboratory tests as well as small and large scale field tests of landfill disposal sludge. Preliminary negotiations are still underway as of October 10, 1974. The EPA project officer for this effort will be Mr. George Huffman.

5.6 Aerospace Water Treatment/Reuse Study

NERC-Corvallis has issued a grant to Aerospace Corporation to determine the implications of open-loop or partially open-loop lime/limestone FGD systems. Under the study, samples of scrubber liquors from three different plants have been obtained, including the following system types:

Eastern (high-sulfur) coal - limestone
- lime

Western (low-sulfur) coal - limestone

The study has the following objectives:

(a) Characterize the constituents in scrubber liquor under various process conditions.

(b) Identify constituents in the liquor that may potentially require control or treatment.

(c) Assess potential liquor treatment alternatives on the basis of treatment efficiency and costs.

(d) Recommend practicable approaches for control and treatment of scrubber liquor for potential reuse or discharge.

The assessment of water treatment systems will cover new technology developments as well as currently operational treatment and control systems. This will include information on the types, sizes, investment costs and operating costs, as well as an evaluation of the technical and economic feasibility of the wastewater treatment and control alternatives. Recommendations will be made for the most practicable approaches to control and treatment of scrubber liquor for water reuse and disposal.

Results of the study could indicate alternate approaches to the sludge disposal problem. One very likely prospect is treatment of filter cake wash from FGD processes producing a mostly gypsum sludge. The EPA project officer for this study is Mr. Dennis Cannon.

5.7 Remarks on the EPA Program

As Sections 5.1 - 5.6 indicate, there are several significant EPA research and development efforts underway at three different research centers. The interrelationship between the various efforts is also described. A substantial amount of close coordination is required for these separate efforts to accomplish the overall task which must be done. This close coordination exists through frequent communication and a spirit of cooperation. The real significance of these efforts, however, is the multi-disciplinary approach to the overall task. Expertise in air pollution control (NERC-RTP), solid waste/residuals management (NERC-Cincinnati) and water treatment/water quality (NERC-Corvallis) have all been brought together in this research and development program. This approach is the only effective way to address environmental concerns.

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FGD SLUDGE FIXATION AND DISPOSAL

by

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The fixation and disposal of by-products produced by Flue Gas Desulfurization (FGD) processes has increased the operational and environmental problems confronting the electric utility industry. As a result of laboratory research and development efforts and pilot plant testing, significant data has been compiled concerning the physical and chemical properties of the sludge. Work to date indicates that stabilization by chemical additives is required and feasible. Technical analysis of sludges from FGD systems stabilized with CALCILOX additives indicate these sludges can be used in a land fill type disposal operation.

Market studies and technical analysis indicate that land fill disposal is the only currently feasible and acceptable disposal method. Land fills constructed with stabilized FGD sludges can meet all engineering, environmental and ecological requirements. In addition, land fill disposal is the only disposal method which can handle the large volumes expected from FGD systems. Full scale disposal operations conducted by Dravo Corporation are described.

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TABLE OF CONTENTS

	Page
List of Tables and Figures	932
Introduction and Background	933
On Going Disposal Research	936
Stabilization and Soil Mechanics	937
Laboratory Testing of Stabilized Sludges	940
General Index Properties	940
Strength Tests	940
Consolidation Characteristics	945
Disposal System Planning	947
Disposal Site Selection	947
Current Disposal Studies	950
Current Projects	951
Cost	952
Summary	953

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LIST OF TABLES AND FIGURES

Table Number	Title	Page
1	Chemical Constituents Desulfurization System Sludge	935
2	Grain Size Distribution Desulfurization System Sludge	938
3	Chemical Constituents of Stabilized Desulfurization System Sludge Leachate	946

Figure Number	Title	Page
1	Solid Waste Products from a 1200 MW Station	934
2	Settling Test Curve	939
3	Effect of Solid Content and Percent Additive on Strength	941
4	Grain Size Curve	942
5	Effect of Various Additives on Shearing Strength	944

FGD SLUDGE FIXATION AND DISPOSAL

INTRODUCTION AND BACKGROUND

After the enactment of the 1970 Amendments to the Clean Air Act of 1967, Dravo Corporation's Research and Development Department began extensive "state of the art" studies of Flue Gas Desulfurization (FGD) systems. One important conclusion of these studies was that although much effort had been directed toward the mechanics of SO_2 removal from flue gases, very little effort had been directed toward the disposal of the FGD systems by-products. Aside from a general knowledge of the chemical constituents of these wastes, no practical data were available concerning the physical and chemical behaviors of these materials and the magnitude of the disposal problems they would create at fossil-fuel-burning generating stations. Realizing the need for additional data to evaluate the alternatives for waste disposal, Dravo Corporation began an extensive study of FGD systems wastes. The major parameters which required identification included:

1) Quantities of wastes to be produced.

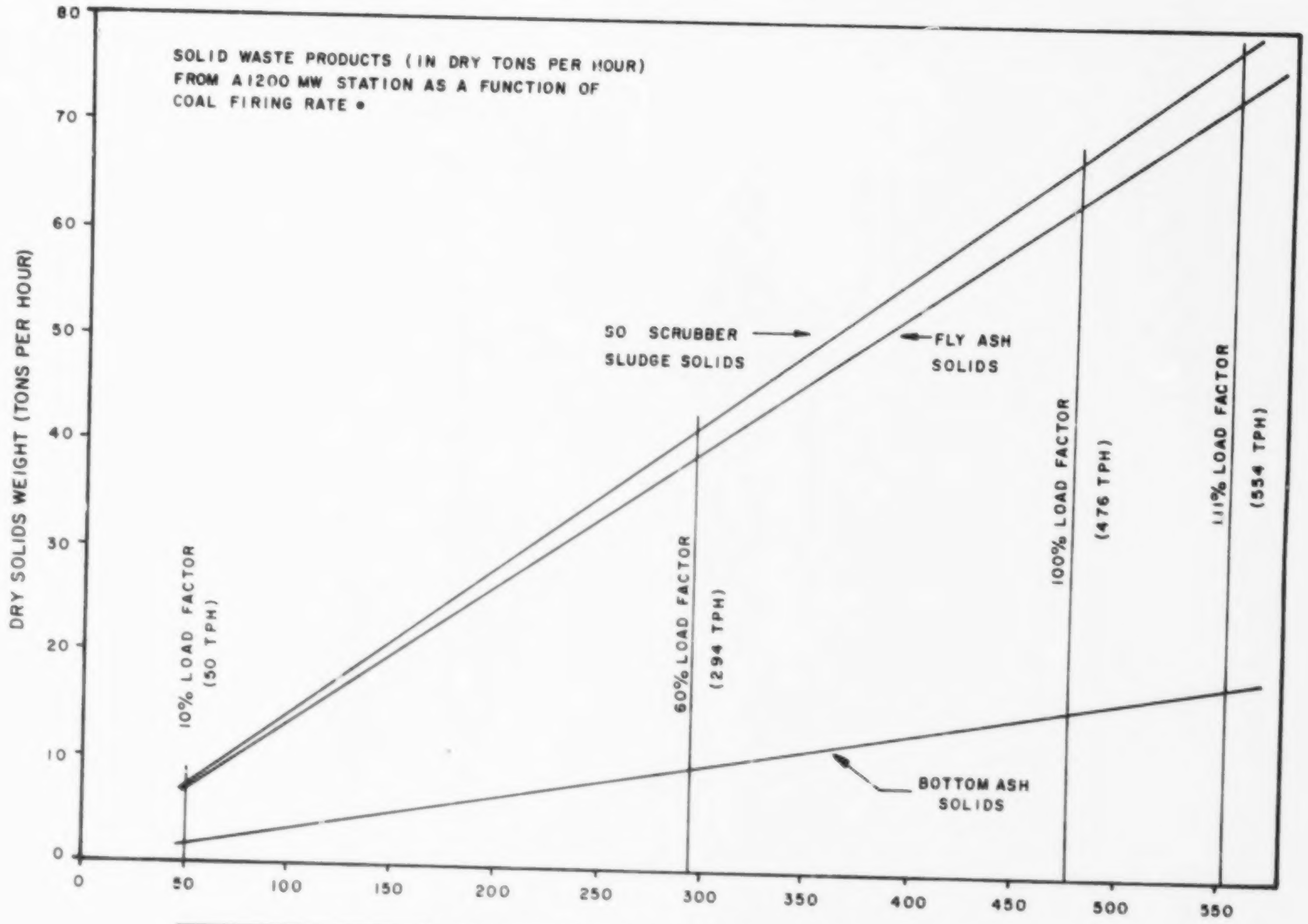
2) Chemical constituents of the FGD wastes.

3) Physical properties of the FGD wastes.

This study lead to the realization that very large quantities of FGD systems wastes would be generated. Figure 1 shows the estimated waste quantities generated by a 1200 MW power station burning high sulfur coal. Although useable products such as light-weight aggregate or road sub-base material could be made from the wastes, marketability studies, existing technology and economic considerations indicated that wastes of this quantity must be placed in land fills.

Evaluation of the chemical constituents of the wastes indicated that the waste solids were generally inert and non-toxic in a controlled environment. Problems could result, however, from the chemical quality of the large quantities of water required in the wet scrubbing method of desulfurization. Reutilization of all the supernatant and leachate from FGD systems wastes was not feasible as the water chemistry after SO_2 removal did not meet the standards required for FGD system makeup water. The water which could not be used had to be treated for reuse, discarded or included in a disposal scheme. A chemical analysis of an SO_2 scrubber sludge from a lime scrubber is shown in Table 1.

Study of the physical properties of FGD systems wastes showed that, due to the particle size, shape and gradation, these materials were thixotropic, i.e., subject to liquefaction.



SOLID WASTE PRODUCTS (IN DRY TONS PER HOUR) FROM A 1200 MW STATION AS A FUNCTION OF COAL FIRING RATE •

DATE 10-3-74
DR ALD CH
REF 2767-2-1

FIGURE 1

• Based on 16.8% Ash and 3.5% Sulfur content of coal with 20%/80% split for bottom ash/fly ash. 100% ash removal and 85% SO_2 recovered.

TABLE 1

Chemical Constituents

Desulfurization System Sludge

Fly Ash	17-20%
$CaSO_3 \cdot 1/2\ H_2O$	65%
$CaSO_4 \cdot 2H_2O$	5-7%
$CaCO_3$	3%
Others	3-5%

Results of the preliminary study indicated that utilization of the FGD systems wastes in stabilized land fill was the only acceptable and economical method of handling the waste problem. Further study of the materials generated in FGD systems determined that, without the aid of a stabilizing agent, the material could not be satisfactorily placed in a land fill. As a result, the series of stabilizing additives known as CALCILOX was developed by Dravo's Research and Development Department. These additives sufficiently alter the properties of the wastes to permit placement in a safe land fill.

ON GOING DISPOSAL RESEARCH

The handling and disposal of large quantities of waste materials generated by FGD systems are directly affected by the inherent physical and chemical properties of the wastes. These properties are a function of the: 1) characteristics of the coal burned; 2) type of boiler; 3) type of scrubber; 4) scrubbing medium; and 5) plant operating procedure. As these variables are unique to each power station, study of the wastes from each station is required to evaluate their properties. Each study should include a pilot FGD system of the type selected for the plant and should be operated under conditions which simulate anticipated conditions during power generation.

Laboratory analyses of the sludges generated by the pilot plant in each study will yield data for evaluation of various disposal methods. A typical laboratory evaluation might include:

1. Bulk density of sludge settled from water slurry
2. Specific gravity of dry solids
3. Particle size, shape and gradation
    a. Wet sieve analysis
    b. Sub-sieve analysis
    c. Scanning electron microscope evaluation
    d. Blaine fineness number
4. Chemical analyses
    a. Sludge solids
    b. Supernatant liquid
    c. Leachate
5. X-Ray diffraction studies
6. Settling tests

7. Filter tests

8. Rheological and pumping tests

Although the sludge generated in each study will be different, test results from several sludges indicate most will have properties comparable to those listed below:

1. Bulk density of settled sludge -
   85 to 95 pounds per cubic foot

2. Specific gravity of dry solids - 2.48 to 2.55

3. Particle size - see Table 2

4. Chemical analyses - see Table 1

5. Settling tests - see Figure 2

To date, Dravo has gathered rheological data on numerous samples of FGD sludges from four different power stations in Pennsylvania, Ohio and West Virginia and has conducted three large-scale (6 and 8 inch pipe diameter) pump loop test programs on FGD sludges.

As a result of extensive rheological testing in the laboratory and in pump loop tests, it has been concluded that FGD systems waste products are suitable for pipeline transport. Although each FGD system sludge has different flow characteristics, they are all non-corrosive, exhibit relatively low abrasion and can be transported over a wide range of tonnages within any given pipe size.

More detailed discussions of the properties of FGD system sludges have been presented by Selmeczi and Knight(1) and by Selmeczi and Elnaggar(2).

STABILIZATION AND SOIL MECHANICS

Once ranges of probable physical and chemical properties of sludges to be produced at a plant have been determined, evaluation of the stabilization characteristics of the sludges is required. Sludges generated in the pilot scrubber should be treated with stabilizing agents such as the CALCILOX series of additives. Testing of the various admixtures of sludges and stabilizing agents will indicate the most economically feasible stabilization procedures for each power station.

Samples should be prepared for continuous monitoring to establish the degree and rate of stabilization. A measure of the degree and rate of stabilization is the resistance to penetration of

TABLE 2

Grain Size Distribution

Desulfurization System Sludge

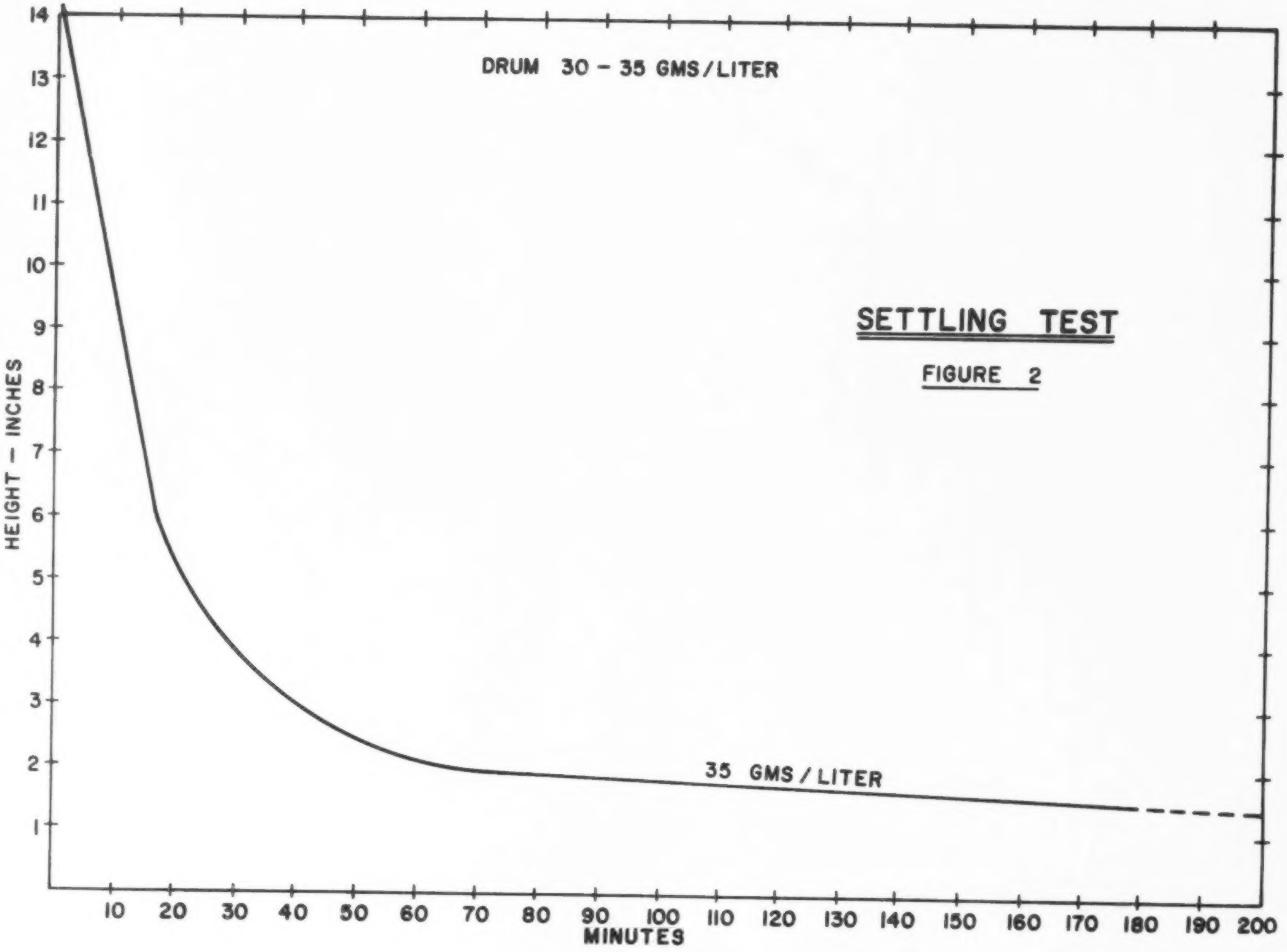
Wet Screen Analysis (Dravo)

+ 50 mesh	-
+100 mesh	1.1%
+200 mesh	4.9%
+325 mesh	9.3%
+400 mesh	14.3%
-400 mesh	85.7%

Sub-Sieve Analysis (Micromeritics Instrument Corp.)

Equivalent Spherical Diameter	Cumulative Wt. %
+18 micron	10%
-18 micron	90%
-12 micron	80%
- 9 micron	70%
- 8 micron	60%
- 6.4 micron	50%
- 5 micron	40%
- 4 micron	30%
- 3 micron	20%
- 1.5 micron	10%

Blaine Fineness Number 7600



SETTLING TEST

FIGURE 2

the treated sludges by a penetrometer. Continuous testing will yield strength-time relationships for samples treated with the various additives. The stabilization test data for sludges treated with CALCILOX H35 are shown on Figure 3. These curves show that strength gain was rapid in some of the samples. Some of the stabilized sludge samples reached the maximum limit of the penetrometer (4.5 TSF) in a few days while others required about four weeks. Based on results similar to those shown in Figure 3, judgment must be exercised in selecting the most promising samples for an extensive testing program. It must be recognized, however, that variables other than sludge properties will affect the degree and rate of stabilization. In addition to the type of additives, consideration must be given to: 1) combinations of additives; 2) quantity of additives; 3) solids content of the sludge leaving the thickener; 4) curing temperature; and 5) slurry pH.

LABORATORY TESTING OF STABILIZED SLUDGES

As the stabilized sludges are new materials and little, if anything, is known about their behavior in a land fill, Dravo Corporation has conducted extensive soil mechanics laboratory tests. The purpose of these testing programs was to develop soil mechanics parameters for correlating the properties of the stabilized sludges with those of known soil types for use in the design of land fills.

General Index Properties

All of the cured, stabilized sludges tested were composed of silt-sized particles; most fall into the ML classification of the USCS classification system. Figure 4 shows a typical particle size distribution of an unstabilized sludge containing 55-60% fly ash. The average particle size of a sludge containing less fly ash would be slightly smaller as calcium sulfite and sulfate crystals generally do not exceed 10 microns in size. Some of the samples exhibited plasticity and were classified as MH.

Natural water contents ranged from 106% (48% solids) to 140% (42% solids). Dry densities of the undisturbed stabilized sludges ranged from a low of 33.1 pounds per cubic foot to a high of 43.7 pounds per cubic foot. Permeability ranged from 1 X 10^{-4} centimeters per second for remolded material to 1 X 10^{-8} centimeters per second for the undisturbed material.

Strength Tests

Undisturbed and remolded stabilized sludges were subjected to direct shear and triaxial shear testing to develop strength parameters for embankment design and to evaluate bearing capacity for a land fill to be used for building sites. A sample of unstabilized sludge was

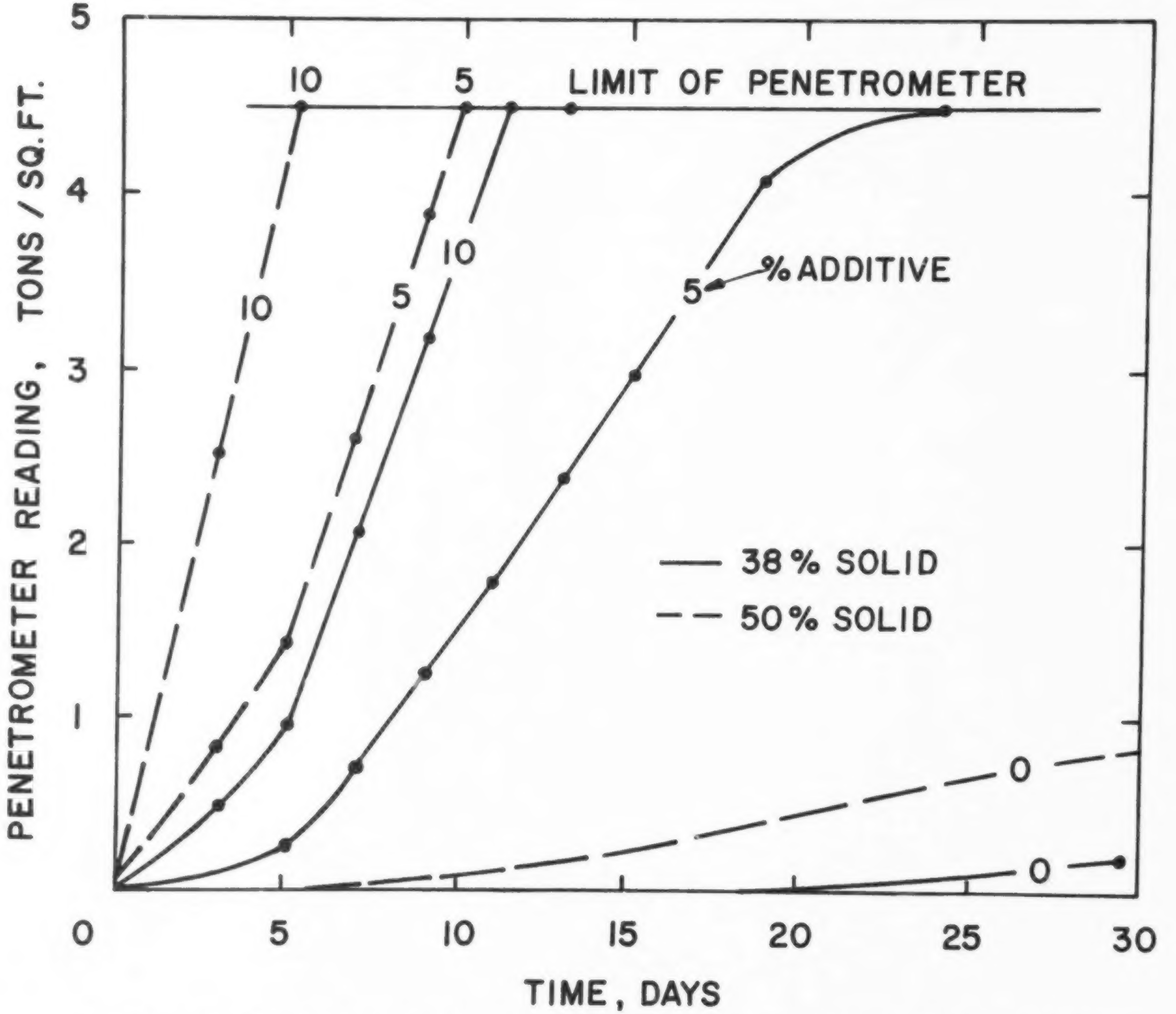
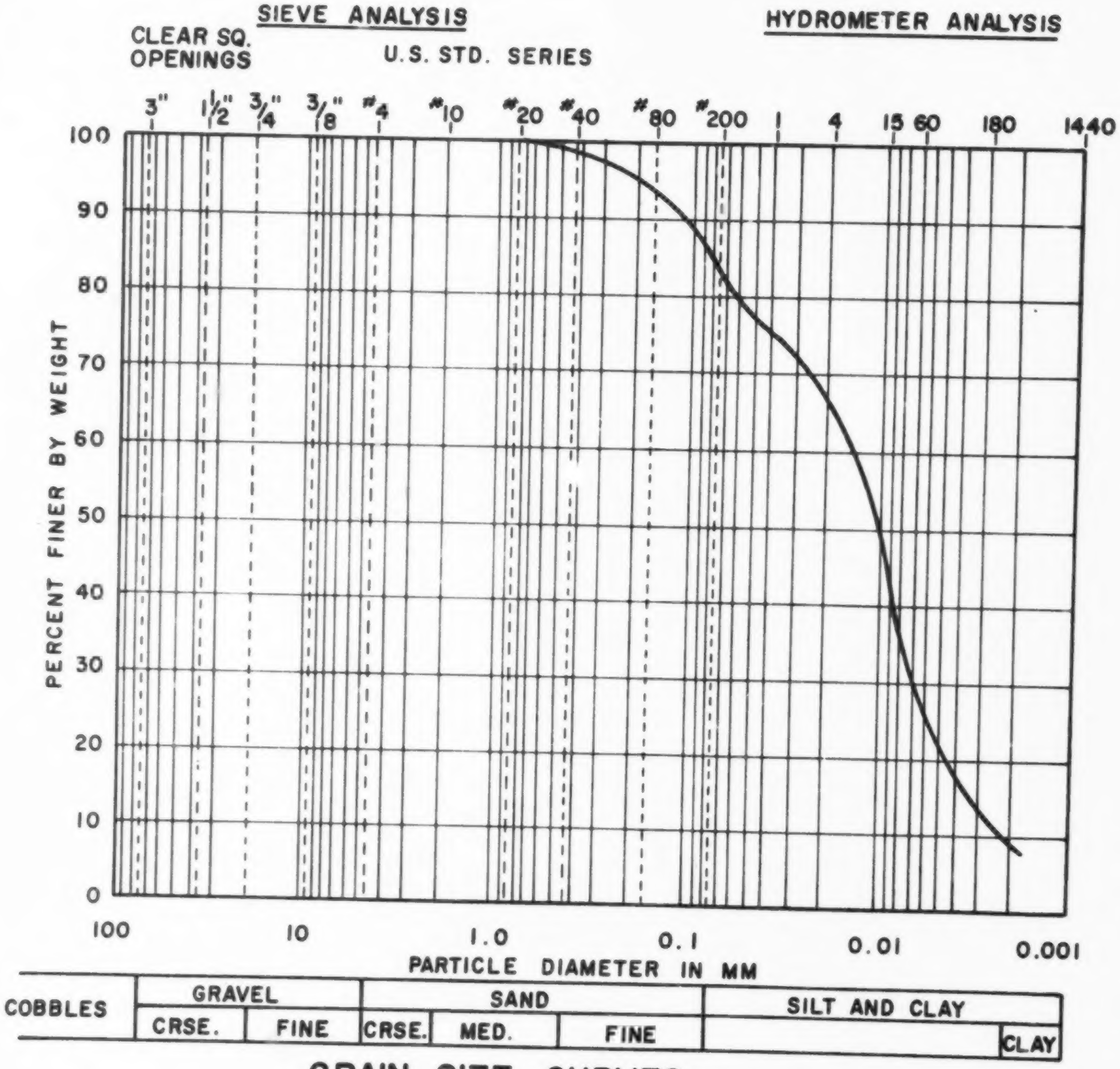


FIGURE 3. EFFECT OF SOLID CONTENT AND PERCENT ADDITIVE ON THE STRENGTH



GRAIN SIZE CURVES
STABILIZED SO_2 SCRUBBER SLUDGE

FIGURE 4

subjected to a direct shear test to evaluate the relative effects of stabilization on the strength of the material.

The angle of internal friction for both the undisturbed and remolded treated materials varied from 37° to 51° with a typical value for a thirty-day cured sludge being on the order of 39°. Most of the samples tested showed very little cohesion. This is to be expected as the low plasticity indicates that the stabilized sludges should behave as granular soils. The untreated sludge exhibited an angle of internal friction between 27° to 30°.

The strength of the stabilized sludges is comparable to that of a dense sand and gravel under static loading conditions while the strength of the unstabilized sludges is similar to that of medium dense sand. It is interesting to note that the stabilized sludges show no significant reduction in strength upon remolding and only a slight reduction upon continued shearing. For example, the peak strength for a thirty-day cured sample (Figure 5) exhibits an angle of internal friction of 40° which was reduced, upon continued shearing, to a residual angle of internal friction of 35.5°. Considering an embankment slope of two horizontal to one vertical under drained conditions, use of the residual strength would provide a factor of safety of 1.4 against slope failure.

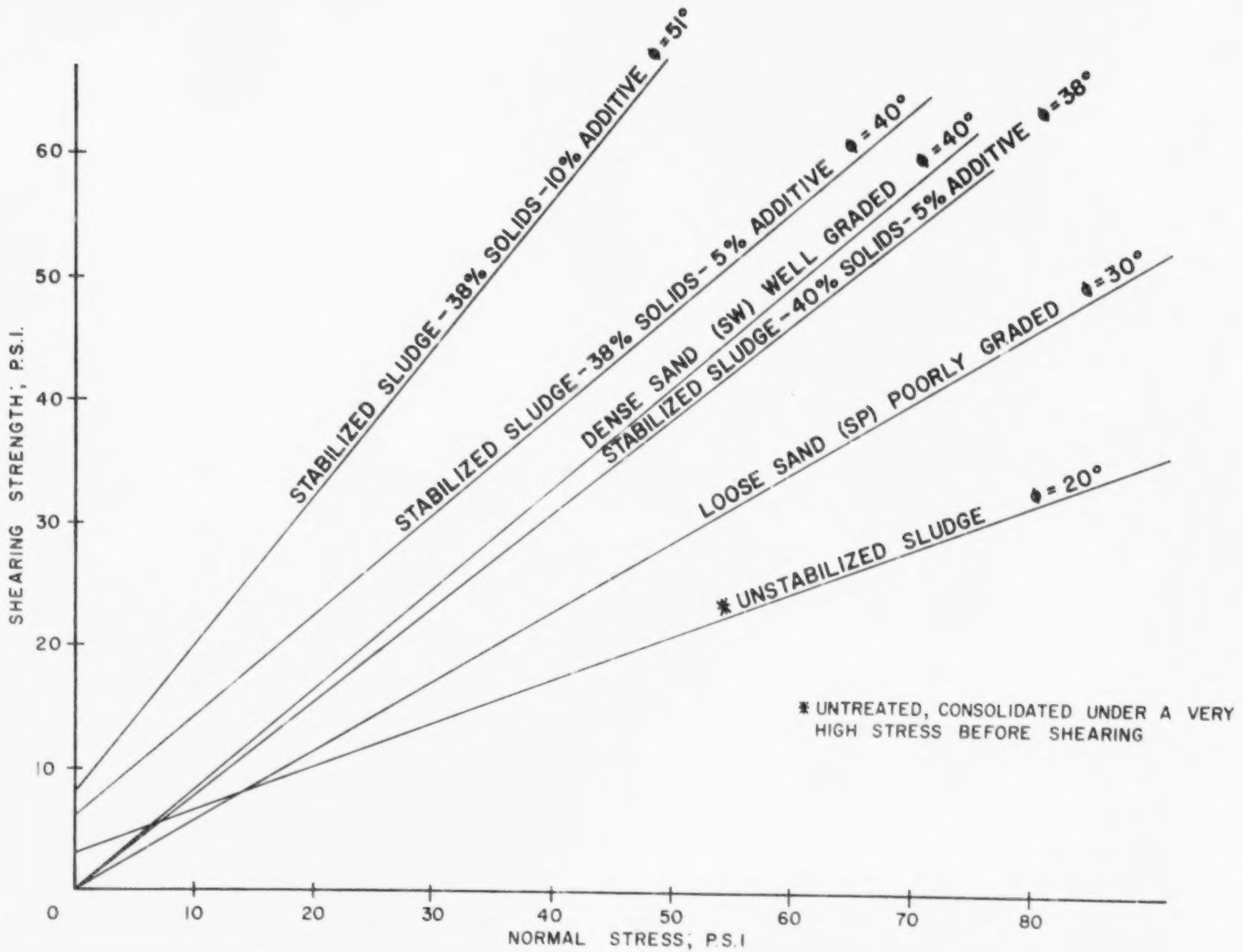
Samples of stabilized sludges consolidated to dry densities greater than 45 pound per cubic foot showed significant increases in strength with increased confining pressures. This may be due to the particles adjacent the failure plane slipping over one another during shear at low confining pressures, while at higher confining pressures the failure plane is forced through individual particles, actually breaking the crystal structure.

Based on these tests, several conclusions can be drawn:

1. The strength of the remolded material is dependent upon the unit weight. For the strength data presented here to be valid, the stabilized sludges must be placed in the disposal area within the range of unit weights that were tested in the laboratory (35 to 50 pounds per cubic foot dry density).

2. Increased solids content of the undisturbed sludges results in increased strength. It will be desirable to stabilize the sludges at the maximum solids content that is practical under operating conditions.

3. Increased curing time results in higher strengths and reduction of natural water content.



EFFECT OF VARIOUS ADDITIVES ON SHEARING STRENGTH

FIGURE 5

4. Increased confining pressures result in a significant increase in strength with stabilized sludges placed at dry densities greater than 45 pounds per cubic foot.

It must be kept in mind that all of these strength data are based on static loading. However, based on the information available to date, there is no significant reduction of strength for samples subjected to vibrating loads in the range of 2 to 5 cycles per second.

Consolidation Characteristics

One-dimensional consolidation tests were run on both undisturbed and remolded samples of stabilized sludges by Dr. Hameed A. Elnaggar of the University of Pittsburgh to determine the consolidation characteristics of the stabilized sludges and to develop the necessary parameters for evaluating potential settlement. The compression index Cc varied from 1.20 to 1.35 for the undisturbed material and from 0.69 to 1.15 for the remolded material. The magnitude of potential virgin settlement is directly proportional to the value of the compression index.

These values to the compression index are relatively high; however, due to the chemical hardening of the sludges, the undisturbed material appears to have a preconsolidation stress of 8 to 10 tons per square foot, the equivalent of the weight of 120 to 160 feet of compacted fill soil. This indicates that relatively high foundation loadings, such as those resulting from multi-story structures, could be placed on the cured sludge with negligible settlement. As the time rate of consolidation is very high, any expected settlement would occur during construction.

If the sludges, after hardening, were to be excavated and then placed as compacted fill, the expected settlement would depend upon the dry densities and moisture contents of the compacted material. Laboratory tests on remolded samples have shown that the magnitude of settlement of structures supported on compacted sludges would be rather high. It is not known if chemical hardening continues after stabilized sludges have been remolded, but if additional hardening does occur, the compressibility of the material may be reduced. More detailed discussions of the properties of stabilized FGD system sludges have been presented by Selmeczi and Elnaggar.(2)

Leachate tests and analyses have also been conducted on stabilized sludges. Below is a typical leachate analysis from a sludge cured for four weeks. Five-hundred (500) grams of the material was slurried with 2000 ml of distilled water and agitated for 48 hours using a Phipps-Bird stirrer. This slurry was allowed to settle for a period of 48 hours and the supernatant decanted for analysis. The results are shown in Table 3.

TABLE 3

Chemical Constituents of Stabilized Desulfurization System Sludge Leachate

pH - 11.6

Dissolved salts - 590 mg/1

Dissolved SiO_2 - Not detectable

Hardness, $CaCO_3$ - 430 mg/1

Fe^{++} - Not detectable

Total iron - Not detectable

Ca^{++} - 172 mg/1

Mg^{++} - .05 mg/1

Mn^{++} - .03 mg/1

Na^{+} - 4 mg/1

Al^{+++} - 4 mg/1

Alkalinity as $CaCO_3$ - 140 mg/1

Cl^{-} - 66 mg/1

$SO_4^{=}$ - 100 mg/1

$SO_3^{=}$ - 92 mg/1

$PO_4^{=}$ - Not detectable

It should be noted in this leachate analysis that the pH is high but all other criteria are within the range of regulatory requirements.

DISPOSAL SYSTEM PLANNING

In the past, long-term (30-40 years) disposal of power plant wastes had not been a part of the planning associated with designing and constructing a fossil fuel power generating station as most utilities considered the disposal of fly ash to be an operating problem. This resulted in the development of numerous short-term disposal solutions which required continuous planning. With the advent of new regulations and public concern on environmental matters, utilities must now develop long-range plans to control their waste by-products, both gaseous and solid.

The planning for FGD waste disposal systems begins at the outfall of the FGD system and progresses through several steps designed to change the material into either a useful product or one which can be disposed of satisfactorily in a land recovery operation. In view of the current state of technology of air quality control systems and the large quantities of material involved, land fill disposal is the best solution. Test data indicate that only stabilized sludges possess adequate strength for a structurally sound land fill.

Rising costs for land, materials and labor make short-term disposal systems economically unattractive. The costs associated with obtaining local and state agency approval are high and the process is generally time-consuming. It will be less expensive in terms of delay time and public antagonism, as well as money, to have one large, well designed and well maintained disposal operation, especially if some beneficial use can be made of the land following completion of the disposal operation. Planning at the outset for a long-term disposal system is the key to long-range disposal economics.

DISPOSAL SITE SELECTION

The largest and most complex task associated with the disposal of SO_2 scrubber wastes in a land recovery operation is the investigation, evaluation and design of the disposal site. To carry a disposal site project from conception to completion requires an interdisciplinary effort utilizing the talents of professionals from design engineers to environmentalists. Studies must be made to evaluate the physical, environmental, sociological, economical and political ramifications of the proposed disposal site.

The disposal area must be designed and constructed to meet all environmental and regulatory requirements. Existing utilities must be relocated or removed as required. The area must be cleared of vegetation. Existing surface drainage must be collected and carried out of the disposal area to prevent disequilibrium of the system water balance or reduction of sludge storage capacity. Numerous other important details must be considered, many of which will vary from site to site.

The relocation of existing utilities such as roads, power lines, pipeline, etc. within the disposal area should be done only as required by the progress of construction and disposal. In this manner negative sociological and economical impacts can be minimized. Clearing of vegetation only as required will help to prevent excessive erosion within the watershed and to maintain the natural aesthetic characteristics which occur within the disposal area.

As most disposal sites will lie in valleys, an embankment will be required to impound the stabilized FGD system sludges. The embankment will retain the sludge during settling, consolidation, curing and stabilization, and will provide a stable and permanent downstream face for the land fill. It should be designed for a full hydrostatic load of unstabilized sludge. Emergency overflow protection through gated or non-gated spillways, decant towers, etc., which meet the requirements of regulatory agencies and good engineering practice during construction and operation of the disposal area should be provided. Normal drainage protection for earth and rock-fill embankments should be provided to control seepage or drainage in the embankment. Standard monitoring equipment designed to evaluate the behavior of the embankment should be installed.

The embankment should be constructed using native materials found in the immediate area. This is the most economical approach, and if the borrow area is located within the impoundment, construction of the embankment will result in increased storage capacity. Embankment construction can proceed in several stages as required by the disposal operation. The final embankment design, however, should be predetermined on the basis of existing foundation conditions and locally available materials.

The natural drainage existing in the disposal area must be controlled by collection or by-passing it through the embankment. This includes both permanent and ephemeral springs and creeks which occur throughout the disposal area. The main conduit through the embankment should be designed to carry runoff from normal rainfall. The runoff from severe storms beyond the capacity of the by-pass system and the precipitation which falls directly on the reservoir surface can be collected in the sludge impoundment area and circulated back to the power plant for make-up water.

A comprehensive evaluation of all factors involved in the disposal area is required to construct and operate a structurally sound, economically feasible and environmentally acceptable disposal site. Items which must be considered during the initial phases of developing a disposal site include:

A. Logistics

    1. Proximity to power station

    2. Availability of property (acquisition of property options)

B. Physical Site Considerations

    1. Reservoir evaluation

        a. Geologic evaluation of site suitability (stratigraphy, structural geology, seismicity, etc.)

        b. Hydrologic evaluation of site suitability (ground and surface water inventory, seepage characteristics of soils and bedrock, water quality, etc.)

    2. Environmental evaluations (environmental impact of disposal on surrounding flora and fauna, land use, etc.)

    3. Archaeological and historical investigations (destruction of some archaeological site)

    4. Etc.

C. Political Considerations

    1. Local government regulations

    2. State government regulations

    3. Federal government regulations

    4. Economic impact of disposal site

    5. Social impact of disposal site

Once the site has been tentatively selected, detailed geologic investigations should be conducted to provide feasibility and design data. This work should include:

A. Detailed Site Investigation

    1. Detailed field reconnaissance to locate borrow areas, seepage areas, abandoned mines, quarries, wells, etc.

2. Drilling program to evaluate foundation conditions in the embankment area, pressure testing for permeability determinations of in-place bedrock, rock mechanics testing for embankment stability, evaluation of rock borrow materials, etc.

B. Preliminary Land Fill Design

1. Design of stable embankment with the materials available.

2. Water balance for disposal area.

3. Relocation and/or removal of utilities.

4. Federal, State and local approval.

    a. Completion of all permits

    b. Submittal and review

    c. Incorporation of regulatory requirements into disposal system design

C. Establishment of Estimated Construction Costs

CURRENT DISPOSAL STUDIES

Dravo is presently studying alternate methods for disposal of FGD wastes. Current research is directed toward more sophisticated dewatering devices and methods in an effort to reduce the quantities and combinations of CALCILOX additives required for stabilization. The results of these studies will include not only better disposal economics, but also better utilization of existing and planned disposal areas.

Studies are also under way to determine the technical parameters involved in the utilization of fossil fuel power plant wastes from existing stations for the construction and operation of the future FGD waste disposal systems.

Research is being conducted to develop more reactive CALCILOX additives in an effort to reduce the quantities of additives required and to improve the characteristics of the stabilized sludge. This research is also aimed at improving the chemical quality of the water in the disposal system.

CURRENT PROJECTS

Dravo Corporation has five FGD disposal projects under contract. Dravo is providing engineering services from conceptual design to final design and construction of an FGD disposal system for a 1760 MW power station located in Pennsylvania. This system is designed to handle 21,000 wet tons per day (FGD system sludge and fly ash) from the power station's FGD system. The disposal system will mix the wastes with the stabilizing additive, transport the slurry approximately seven miles by pipeline, and deposit it behind a 400-foot high embankment. The slurry and additive will cure behind the embankment and form a stabilized land fill mass. At the completion of this long-term disposal project (30 years) the disposal area can be used for a light industrial development, a recreational area or a man-made lake. The ultimate utilization of the land can be left to the local municipailties as the various options remain open to completion of the land fill operation.

Dravo recently completed a stabilization demonstration program at another Pennsylvania power station. The FGD system at this station handled an output of approximately 125 MW. For the same utility, Dravo is conducting a study to develop a disposal system with the capacity to handle the wastes from FGD systems for a total output of 900 MW, 400 MW from one station and 500 MW from another. The expected output from these two stations is 7200 wet tons per day. This study will develop a conceptual design, locate potential disposal sites and develop basic economics of the disposal system.

Dravo is also assisting a California utility with on-going tests of a stabilization demonstration project. The disposal system was designed by Dravo and testing began early in 1974. The system handles the FGD system waste from a proto-type SO_2 scrubber with a stack gas flow through equivalent to a 150 MW generating unit burning low sulfur coal. This project is demonstrating the importance of make-up water and sludge chemistry in the FGD disposal system.

Dravo is currently under contract to provide detail design of a disposal system for a 1236 MW power station located in West Virginia. The system will provide disposal for the wastes produced by a total plant FGD system. The disposal system will be designed to handle 5500 wet tons per day of waste solids in a slurry form which will be mixed with the stabilizing additive CALCILOX and transported via pipeline to the land fill disposal area. This system will also utilize 1900 dry tons per day of other power station waste materials in the construction of the disposal area.

Another Dravo project currently underway is the detail design of an FGD waste disposal system for an Ohio utility. The power station capacity is 820 MW and the expected maximum waste quantity is 7700 wet tons per day. The wastes will be received in slurry form, mixed with the stabilizing additive, and transported by pipeline to the land fill disposal area. A unique feature of this project is that the disposal sites under consideration are in strip and deep mined areas.

COST

The cost for FGD waste disposal systems vary considerably and depend on such factors as waste quantities, design life of the disposal area, site logistics, power plant size, location, population density and area development. It is clear, however, that the best economics for disposal systems are developed by early planning of long-term disposal systems where capital investments can be spread over large disposal tonnages.

Present estimates indicate that long-term disposal system capital investments will be in the range of 30 million dollars but can be as high as 60 million. When these long-term investments are reduced to unit costs, economic studies indicate that SO_2 sludge disposal systems will cost in the range of 2 to 4 dollars per ton of coal burned. These are estimates of the total cost for a long-term disposal system designed to handle fly ash and bottom ash as well as FGD system sludges. They include costs for conceptual development, site investigations and evaluations, land acquisition, capital costs of the system hardware and operating costs. No attempt has been made to reduce these estimates by the ultimate salvage value of the reclaimed land upon completion of the disposal operation.

SUMMARY

The current public awareness of the environment and new federal regulations dealing with air quality have forced the power industry to increase their efforts to control objectionable emissions. Although their efforts have been successful in reducing air pollution, the power industry is now faced with a waste disposal dilemma. With the introduction of flue gas SO_2 removal, the quantities of waste have increased several orders of magnitude, but the technology for handling these wastes is almost non-existant. In spite of this, Federal, State, and local regulatory agencies demand an immediate and satisfactory solution.

Until recently, very little was known about the physical and chemical characteristics of the SO_2 wastes. Realizing this deficiency, Dravo Corporation began a series of studies to identify the magnitude of the waste quantities as well as the physio-chemical parameters which would best describe them. Although it is technically feasible to turn these wastes into useful manufactured products, the enormous quantities of these wastes make disposal rather than utilization the only economically feasible solution.

Dravo Corporation has conducted an intensive research effort designed to identify the physical and chemical characteristics of these new wastes with regard to placing them in a land fill. In order to make this type of operation meet the stringent environmental regulations which now exist and those which will no doubt be enacted in the future, Dravo developed a series of additives called CALCILOX which turn the thixotropic, calcium sulfite-sulfate slurries into reasonably high strength, low permeability materials. The feasibility of this solution has been tested on a proto-type installation and will soon be used in a large, 21,000 wet tons per day, disposal operation. Studies for other disposal operations of a similar magnitude are in various phases of completion.

All currently available data indicate that costs for a long-term disposal system, from conception to final design and construction, will be on the order of 2 to 4 dollars per ton of coal burned. Dravo Corporation is continuing its research in an effort to find more economically attractive solutions to the problems of FGD wastes disposal.

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UTILIZING AND DISPOSING OF SULFUR PRODUCTS FROM FLUE GAS DESULFURIZATION PROCESSES IN JAPAN

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Flue gas desulfurization in Japan has so far been oriented toward processes which by-produce salable products. The by-product sodium sulfite has reached 350,000 tons/year and has already filled the demand. The capacity of the by-production of sulfuric acid will reach 1,000 tons/day in 1975. Gypsum is considered to be the most rational by-product because of the increasing demand for wallboard and cement; the production capacity will reach 6,000 tons/day in 1975. Sulfur has been by-produced in relatively small plants. The production of ammonium sulfate is under consideration. However, since so many FGD plants are to be built, it is likely that in the future supply of the by-products will far exceed the demand. New uses of gypsum has been studied extensively.

UTILIZING AND DISPOSING OF SULFUR PRODUCTS FROM FLUE GAS DESULFURIZATION PROCESSES IN JAPAN

I Introduction

Recently in Japan about 6 million tons yearly of SO_2 have been emitted mainly by the burning of heavy fuel oil. Desulfurization efforts have been made in earnest since 1966. Among various desulfurization processes, those which first became popular were hydrodesulfurization of heavy oil by-producing elemental sulfur and sodium scrubbing of waste gases by-producing sodium sulfite (Figure 1). A wet lime process plant by-producing salable gypsum has been in operation since 1964 but it was not until 1972 that construction was started on many plants by-producing gypsum. Processes that give by-product sulfuric acid, elemental sulfur and calcium sulfite have been developed since 1971. The discarding of calcium sulfite sludge is not as widespread in Japan as it is in the United States, because of the limitations in land space available for disposal.

However, since many desulfurization plants are to be built, it is likely that in the future the supply of the by-products will far exceed the demand, necessitating the discarding of a substantial portion of them. Gypsum is generally considered to be the most reasonable by-product because of the increasing demand for it and also because of the ease with which it can be discarded. The various by-products from waste gas desulfurization processes are discussed below.

II Sodium sulfite

The sodium scrubbing processes by-producing sodium salts were reported on by the author at the EPA FGD symposium last year[1]). The reasons for the rapid development of the processes are the simpleness of the processes and the usefulness of the by-product sodium sulfite for paper mills. More than one hundred plants have been installed mainly for relatively small gas sources, industrial boilers, chemical plants, etc. Yearly production of sodium sulfite has reached 350,000 tons and has already filled the demand resulting in a decrease of the selling price (Figure 2). Nevertheless, the SO_2 recovered as sulfite is only 4% of the total emission. Asahi Glass Co. recovers SO_2 from a glass furnace to produce sodium sulfite, which is oxidized into sulfate and returned to the furnace. There is not much demand for sodium sulfate, either. Several smaller plants produce waste sodium sulfite or sulfate solution. Not many additional sodium scrubbing plants are expected to be built in the future.

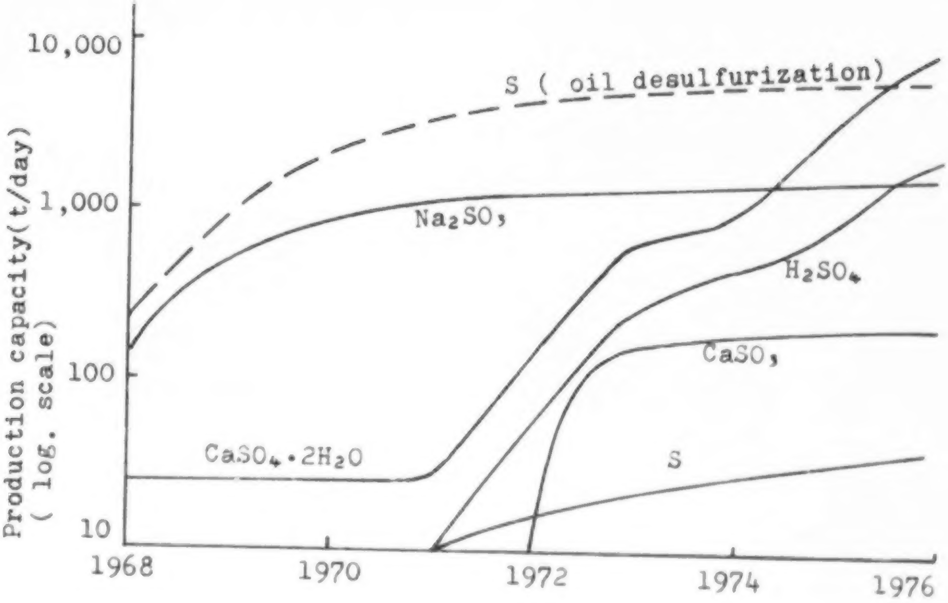


Figure 1 Production capacity of waste gas desulfurization

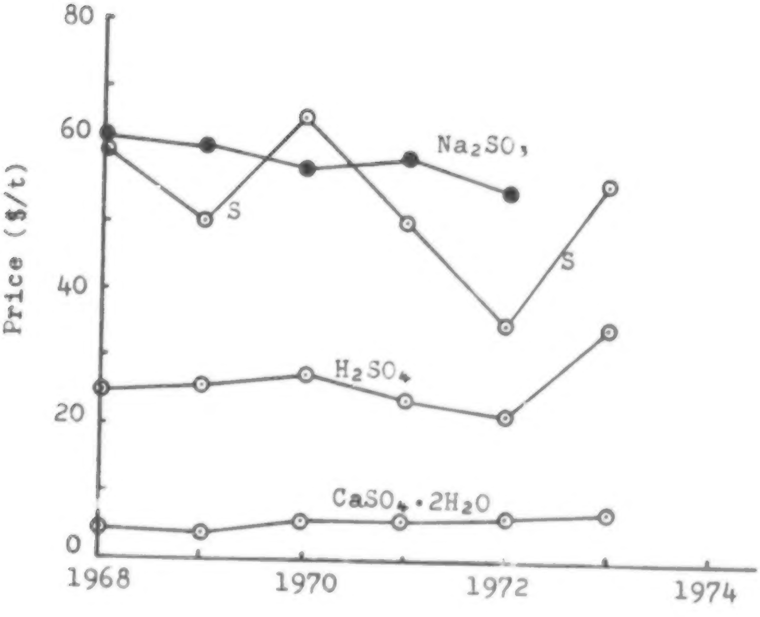


Figure 2 Price of by-products

III Sulfuric acid

The supply and use of sulfuric acid in Japan are listed in Table 1. Pyrite, which was the major source of the acid, has been gradually replaced by smelter gas and sulfur. The production of the acid by flue gas desulfurization was begun in 1971. The production capacity will reach 1,000 tons/day in 1975. But continuing rapid development cannot be expected because the increase in the demand is only 200,000-300,000 tons yearly.

Table 1 Supply and use of sulfuric acid in Japan (1,000 tons)

	1971	1972	1973
Supply			
Smelter gas	3,470	4,203	4,789
Pyrite	3,620	2,600	1,881
Sulfur	146	442	950
Others	72	140	164
Total	7,308	7,385	7,784
Use			
Fertilizer	2,418	2,579	2,560
Others	4,921	4,984	5,623
Total	7,339	7,563	7,823

The Wellman-Lord process has been the major process for the production of sulfuric acid. At present, there are five plants in operation that use the process and seven plants under construction. The sulfuric acid production capacity of those plants will reach 840 tons/day by the end of 1975. The main problem concerning the process is wastewater treatment. At the Nishinagoya plant of Chubu Electric (220MW), a portion of absorbing liquor is cooled to 0°C to crystallize out the sodium sulfate, which is separated by a centrifuge. The sulfate, which contains some sulfite, is dissolved in a purge stream from the prescrubber, treated with sulfuric acid to eliminate any sulfite, aerated, oxidized with ozone, settled to precipitate solids, neutralized with sodium hydroxide, and then discharged to sea. The chemical oxygen demand of the discarded water is kept below 10ppm, which is required by regulations. portion of the separated sodium sulfate is sold to the chemical industry.

An SO_2 recovery plant by the Sumitomo activated carbon process has been in operation at the Sakai Power Station of Kansai Electric, treating 90,000scfm of flue gas from an oil-fired utility boiler. One advantage in producing sulfuric acid from the recovered SO_2 by the Wellman-Lord and Sumitomo processes is the small size of vessels used for the acid production due to the high SO_2 concentration of the gas to be fed into the acid plant--nearly 100% for Wellman and 10-20% for Sumitomo as compared with 6-10% for the gas by pyrite or sulfur burning. There is no further plan, however, to install a larger carbon process plant.

Two magnesium scrubbing plants respectively using the Mitsui Mining process and Onahama-Tsukishima process have been in operation. Both are installed in copper smelters with sulfuric acid plants. The former treats 44,000scfm of tail gas from a sulfuric acid plant and the latter treats 49,000scfm of converter gas containing 2% SO_2. The recovered SO_2 is sent to sulfuric acid plants.

IV Elemental sulfur

Recently in Japan the supply of elemental sulfur has been depending mainly on the by-product from the hydrodesulfurization of heavy oil (Table 2).

Table 2 Supply of and demand for sulfur (in 1,000 tons)

		1972	1973	1974 (estimate)
Supply	Mined	12	0	0
	Recovered	622	761	880
	Imported	13	65	66
	Total	647	826	946
Demand	Use	606	753	836
	Export	53	62	63

There are currently four processes being used to by-produce sulfur by waste-gas desulfurization: (1) the Wellman-Lord process with a Claus furnace, (2) the Shell process with a Claus furnace, (3) ammonia scrubbing with an IFP reactor, and (4) magnesia scrubbing with a Claus furnace. A plant with the process (1) has been in operation since 1971 at the Kawasaki plant of Toa Nenryo, treating tail gas (39,000scfm) from a Clause furnace containing 6,000ppm SO_2. Two plants respectively using the processes (2) and (3) have started operation recently; the former at the Yokkaichi plant of Showa Yokkaichi Oil, treating flue gas (64,000scfm) from an oil-fired industrial boiler and the latter at the Shimozu plant of Maruzen Oil, treating tail gas (24,000scfm) from a Claus furnace. A plant with the process (4) will start operation soon at the Chiba plant of Idemitsu Kosan, to treat 275,000scfm gas from a Claus furnace and an industrial boiler. The recovery of SO_2 from tail gas of the Claus furnace to return to the furnace may be made fairly economically, but the by-production of sulfur at power plants would be costly. The sulfur by-producing processes will be further developed when the oversupply of other by-products becomes obvious.

Elemental sulfur has also been recovered by the hydrogen sulfide recovery processes. By the Takahax process a fine powder of sulfur is obtained which is intended for use in agricultural chemicals. Not many new uses for sulfur have been studied in Japan as they have been in the U.S.A.

V Ammonium sulfate

Ammonium sulfate was produced until recently at the Yokkaichi Plant of Chubu Electric using the Mitsubishi manganese process. The plant discontinued operation recently because of the difficulty of removing more than 90% of the SO_2 in flue gas and the economical disadvantage.

Until a few years ago there were several ammonia scrubbing plants treating tail gas from sulfuric acid plants to by-produce ammonium sulfate. All of the plants were shut down because of the oversupply of ammonium sulfate. Now there are a few small ammonia scrubbing plants treating flue gas to produce a dilute ammonium sulfate solution to be discarded. The discarding of ammonium sulfate solution is to be restricted because it can cause a eutrophication problem. Due to the present shortage of nitrogen fertilizers in developing countries, Nippon Kokan is now considering building an ammonium scrubbing plant at its Fukuyama Works to by-produce ammonium sulfate for export. Nippon Kokan has already developed a process by which SO_2 in waste gas and ammonia in coke oven gas are both recovered to produce ammonium sulfate2). There is some doubt, however, as to whether a market for ammonium sulfate can be secured until several years from now. Another problem in ammonia scrubbing is the plume formation. Nippon Kokan is considering the use of an electrostatic precipitator for plume prevention. The plume can be prevented by the use of an acidic solution as an absorbing liquor, as is being done with Kurabo's acidic ammonium sulfate-lime process4).

VI Calcium sulfite

Not much calcium sulfite has been produced in Japan because of the limitations on the use and on the landspace available for discarding it. Mitsui Aluminum Co., which has produced calcium sulfite sludge since 1972, is going to use the gypsum production process for new installations because of the poor nature of the sludge. There is no focus on sludge stabilization, as there is in the U.S.A.

The calcium sulfite obtained by the wet lime processes usually consists of very small crystals about 0.1 micron in thickness and about 1 micron in length and is not easy to filter. The calcium sulfite from the sodium-limestone processes of Showa Denko and Kureha-Kawasaki grows into much larger crystals about 1 micron in thickness and 10 to 30 microns in length. At the Saganoseki Smelter of Nippon Mining Co., the sulfite obtained by the Showa Denko process is filtered by a vacuum filter, mixed with copper ore, and is fed into a smelter to recover SO_2. Also for discarding, the sulfite by the sodium-limestone process might be better than that by the wet lime process.

A synthetic paper from fairly pure calcium sulfite and polyethylene, at a weight ratio of about 70:30, has been produced recently by Lion Fat and Oil Co. jointly with Idemitsu Kosan. This new product has some defects and is now under improvement.

VII Gypsum

Demand for and supply of gypsum Most of the big SO_2 recovery plants now under construction or being planned are oriented toward the by-production of gypsum for the following reasons: (1) Japan has plenty of limestone. (2) Other by-products such as sodium salts, sulfuric acid, and ammonium sulfate will not increase much since they are already in oversupply. (3) Production of elemental sulfur from SO_2 in waste gases is not very easy. (4) Japan does not have much available land on which to dump calcium sulfite sludge. (5) Demand for gypsum has been increasing considerably. (6) Gypsum is suitable for discarding in the case of oversupply.

The demand for and supply of gypsum in Japan is illustrated in Figure 3. All of the by-product gypsum has been used so far for wallboard production and as a retarder for cement setting because there has been a slight shortage of gypsum in Japan since 1971. But since so many desulfurization plants by-producing gypsum are to be installed, oversupply of gypsum is considered likely to occur in the future. The processes and installations by-producing gypsum are described in the author's other paper for the present symposium[4].

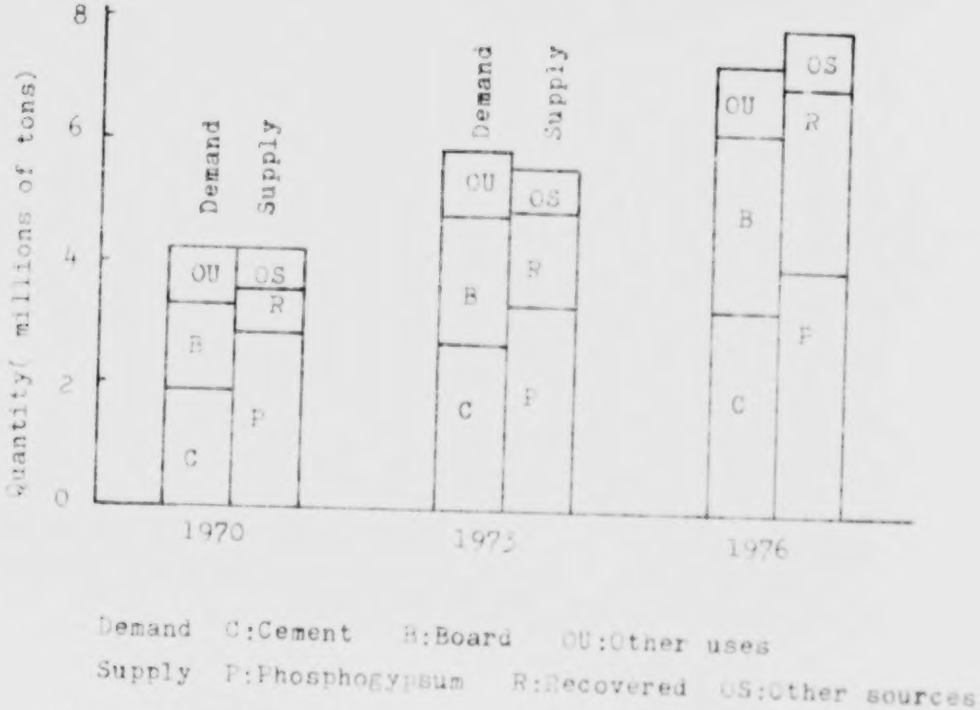


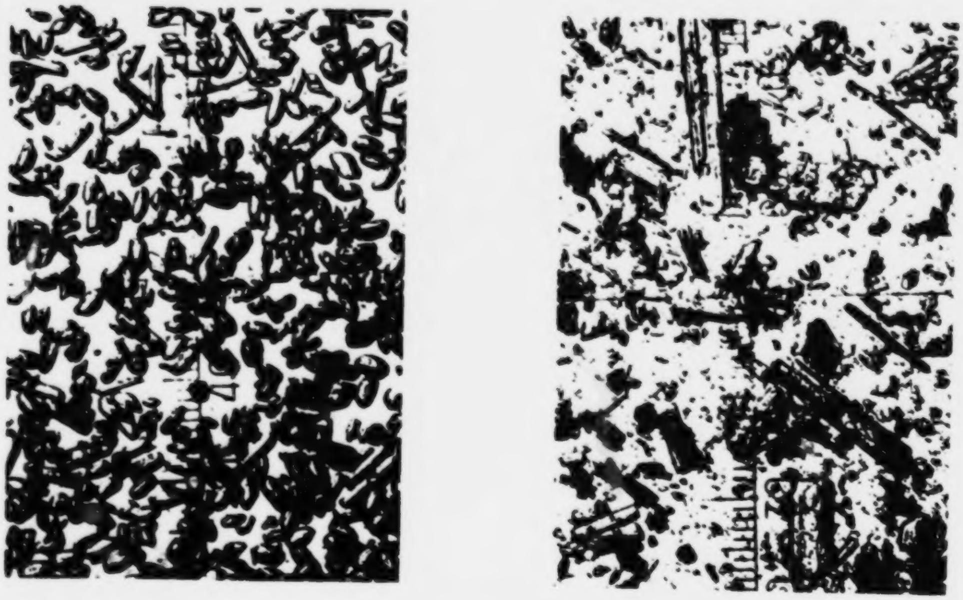
Figure 3 Demand for and supply of gypsum in Japan

__Use of gypsum for wallboard and cement__ For wallboard production, an appropriate crystal size (larger than about 30 microns in length and more than about 10 microns in thickness) and low impurity are favored. Gypsum obtained from oil-fired flue gas usually meets these requirements. (Photographs A-F).

The by-product gypsum from oil-fired boiler flue gas is nearly white or light brown in color. Most of the wet lime-limestone process plants in Japan have a cooler or a prescrubber of flue gas where the gas is sprayed with water for cooling as well as for humidifying and removing most of the dust which was not caught by an electrostatic precipitator.

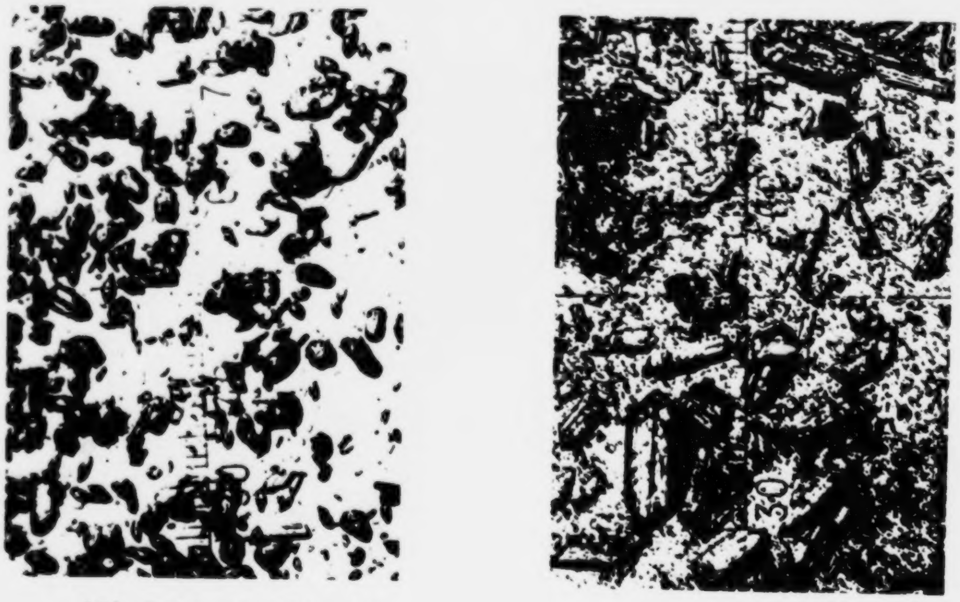
Dark colored gypsum, since it contains a considerable amount of carbon dust, has less commercial value. The gypsum obtained at a new plant of Mitsui Aluminum Co. from coal-fired boiler flue gas passing through an electrostatic precipitator by the Mitsui Miike limestone process (which

Photomicrograms of by-product gypsum (x 100)



(A) Mitsubishi-JECCO
($CaCO_3$ scrubbing)

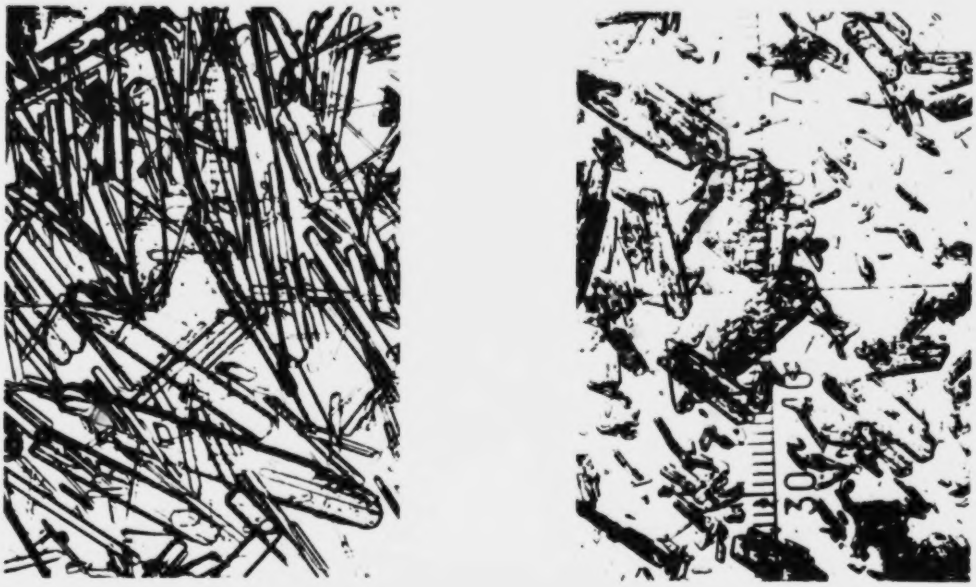
(B) Mitsubishi-JECCO
($Ca(OH)_2$ scrubbing)



(C) Babcock-Hitachi
($CaCO_3$ scrubbing)

(D) Chiyoda
(H_2SO_4-$CaCO_3$)

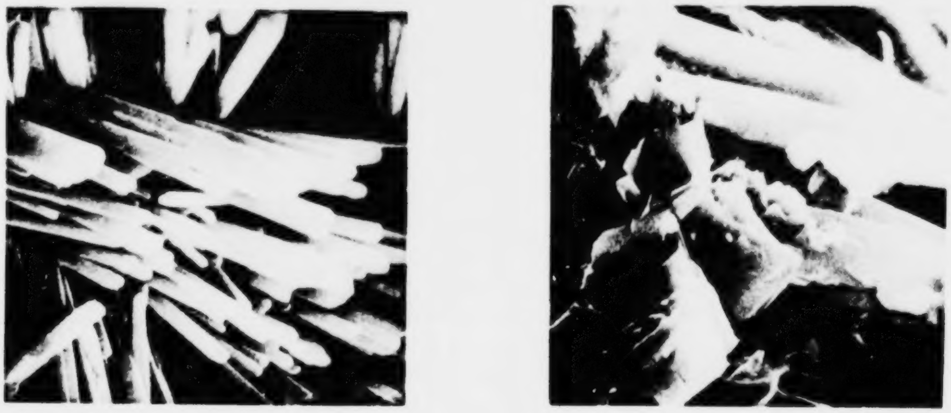
Photomicrograms of by-product gypsum (x 100)



(E) Kureha-Kawasaki)
(Na_2SO_3-$CaCO_3$)

(F) Nippon Kokan
($(NH_4)_2SO_3$-$Ca(OH)_2$)

Scanning type electron photomicrograms of the broken surface of a piece of gypsum(G) and GPC(H) (x 1,500)



(G) Gypsum

(H) GPC

has no prescrubber) contains about 10% fly ash and some carbon and is gray in color. The gypsum has been tested by the sister company, Mitsui Toatsu Chemicals, for wallboard production. Similar gypsum to be obtained at the Takasago Power Station of Electric Power Development Co., will possibly be used for cement.

For use as a retarder in cement setting, gypsum should contain less than about 10% moisture because wet gypsum tends to form a "bridge" in the hopper and cannot be charged smoothly to the cement mill. Normally the by-product gypsum contains less than about 10% moisture after being centrifuged. Well-grown gypsum produced by the sodium-limestone process (100-500 microns, Photograph E) contains only 5 to 7% moisture after being centrifuged. Presence of sodium in gypsum can adversely affect the property of cement but sodium in gypsum produced by the sodium-limestone process is in a negligible amount because of the simplicity of washing due to the large crystal size. Fly ash, about 10% in gypsum, has no bad effects. Calcium sulfite can be used also for a retarder in cement setting replacing a portion of gypsum.

The Kashima Station of Tokyo Electric Power has produced powdery gypsum at a 150MW plant by the reaction of powdered limestone with dilute sulfuric acid (15-20%) obtained by a water wash of carbon which has absorbed SO_2. The filtrate from the gypsum centrifuge has to be discarded because its circulation in the washing produces solid deposits of the carbon decreasing its activity.

As an alternative, the station has recently operated a 15MW test unit where the acid is concentrated to 50-70% by contact with the hot flue gas from an electrostatic precipitator and then treated with powdered limestone. By the heat from the reaction most of the water is eliminated to produce nearly dry gypsum, which is extruded to form pellets about 20mm in diameter and 50mm long. The pellets are suitable for charging into cement mills and also might be suitable for landfill or disposal.

Gypsum for building material As a considerable oversupply of gypsum may occur in the future, new uses of gypsum have been recently studied by many organizations. The most promising new use is as a building material. The usual type of calcium sulfate hemihydrate (β type) has a lower strength than concrete (Figure 4). The hemihydrate of α type has a much larger crystal size and higher strength than β type but is fairly expensive. The form II anhydrite which is obtained by heating gypsum at 950-1,000°C hydrates fairly rapidly when a small amount (1-2%) of potassium sulfate is added and increases the strength. Recent tests by Onoda Cement Co. have shown that an anhydrite of good quality can be obtained with by-product gypsum from SO_2 recovery if the fly ash content is less than about 5%. A larger amount of fly ash tends to decrease the strength.

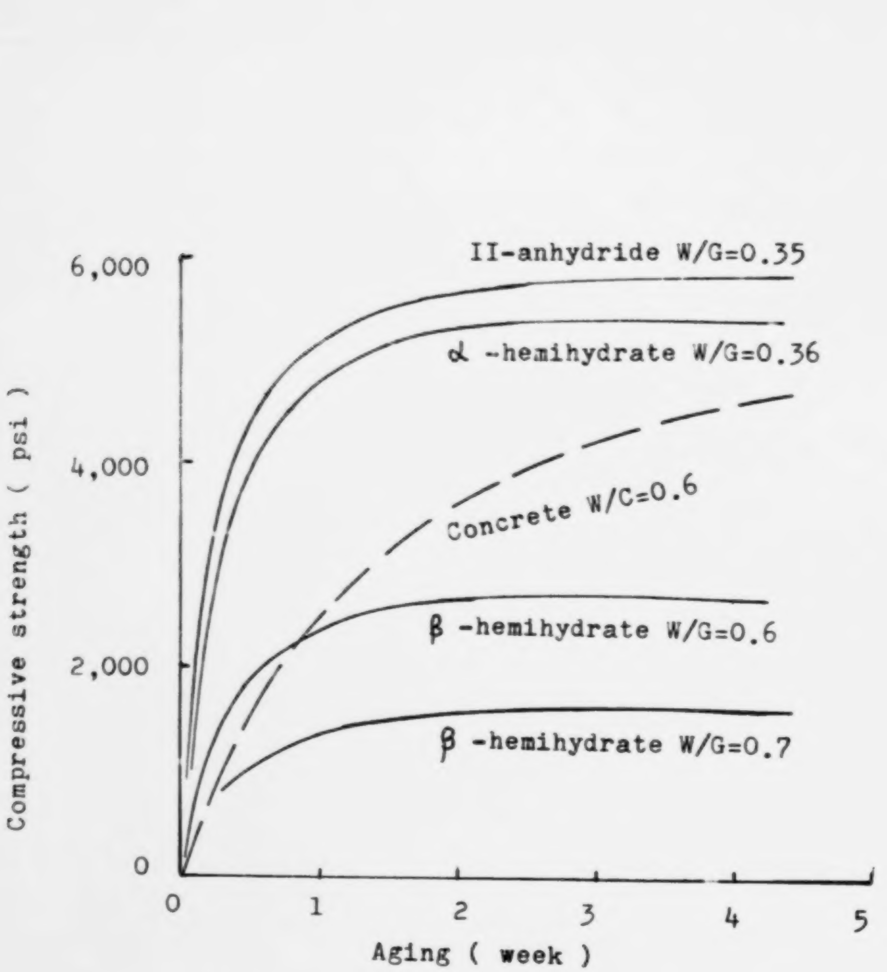


Figure 4 Strength of various types of gypsum and concrete (W/G and W/C mean weight ratio of water against gypsum and cement, respectively)

Technology for reinforcement of gypsum with glass fiber has been developed recently in England[3]. The reinforced gypsum from α type hemihydrate has an equal compression, bending, and tensile strength and much higher impact strength when compared with asbestos-reinforced concrete.

Gypsum plastic composite An important defect of gypsum as a building material is its lack of resistance to water. To eliminate this weakness, gypsum plastic composite (GPC) has been recently developed in Japan through the cooperation of Mitsui Toatsu Chemical and Taisei Construction Co. (Figure 5). Usually a resin monomer such as methyl methacrylate (MMA) or styrene is used for impregnation. The monomer is polymerized by a thermal catalytic means. Some results of tests with MMA are shown in Tables 3 and 4. GPC has superior qualities in its strength, resistance to water, acid and base, and also in its good workability and semi-incombustible property. It may, therefore, be used as a high-grade building material.

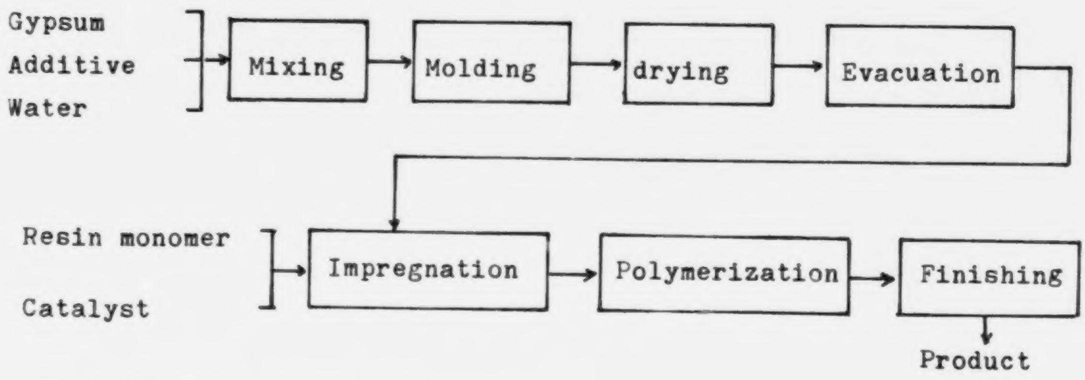

Gypsum
Additive
Water
Mixing
Molding
drying
Evacuation
Resin monomer
Catalyst
Impregnation
Polymerization
Finishing
Product

Figure 5 Process for GPC production

Table 3 Blending of materials

No.	β-hemihydrate	Glass fiber	Water	MMA
A	100	0	57	0
A'	100	0	57	35.5
B	100	3	63	0
B'	100	3	63	38.1

Table 4 Properties of gypsum and GPC

No.	Specific gravity (G/ml)	Compressive strength (psi)	Bending strength (psi)	Wearing (mils/1,000 revolutions)
A	1.274	1,870	740	360
A'	1.699	10,200	2,780	32
B	1.214	1,410	966	720
B'	1.663	11,220	3,890	44

Observations of the broken surface of pieces of ordinary gypsum and GPC by a scanning type electron microscope have shown that for gypsum, crystals were not broken but came apart from each other by stress, while for GPC, each crystal was broken requiring a great stress (Photograph H). This explains the high strength of GPC.

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TVA-EPA STUDY OF THE MARKETABILITY OF ABATEMENT SULFUR PRODUCTS

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CONTENTS

Page

Introduction 972

Results of the Phase I Study 973

Preliminary Feasibility Study of Calcium-Sulfur Sludge Utilization in the Wallboard Industry 998

Phase 2 of the TVA-EPA Study of the Marketability of Abatement Products 1000

TVA-EPA STUDY OF THE MARKETABILITY OF ABATEMENT SULFUR PRODUCTS[1]

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ABSTRACT

During the past year a hypothetical study of the potential for marketing abatement sulfuric acid produced from SO_2 which is emitted by the power plant stack gases from seven TVA coal-burning steam plants was made in cooperation with EPA. A production-distribution model was developed on a time-sharing computer to determine maximum net sales revenue to the utility from sales of sulfuric acid to the relatively inefficient, high-cost sulfuric acid producer. The results of the study indicate that for the approximately 2 million tons of sulfuric acid that could be produced annually by TVA, the net sales revenue above distribution costs only would be approximately $8.75 per ton. If TVA were to use 10 percent of the acid at Muscle Shoals for the production of wet-process phosphoric acid or other fertilizer, the net sales revenue would be increased approximately 50 cents per ton of sulfuric acid.

Based on the above results an expanded study has been initiated to determine for specific power plant installations the potential net sales revenue for byproduct elemental sulfur and sulfuric acid which can be realized from marketing strategies covering the existing acid market, the existing elemental sulfur market, and growth markets for such commodities. This study should have general application for the geographic area located east of the Rocky Mountains in the United States. The effect of marketing abatement production of sulfuric acid and/or elemental sulfur on existing production-shipment-consumption-pricing patterns will be simulated using the production-distribution model developed in Phase I. The expanded model will be developed on a time-sharing computer which facilitates access for any specific company.

At the same time a second study was conducted on the potential marketability of abatement calcium sulfate production. That is, instead of discarding calcium-sulfur sludges, if the sulfur dioxide is recovered as gypsum, it may be possible to sell it to the wallboard industry.

Depending on the power plant location and processing costs, this advantage over a throwaway process could range from nothing to over $16/ton of gypsum disposed. For a 500-MW power unit, this could be as much as a $3.8-million-per-year reduction (45%) in the cost of operating a lime-scrubbing, solids-throwaway system.

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[1] To be presented at the Flue Gas Desulfurization Symposium, Atlanta, Georgia, November 4-7, 1974.

TVA-EPA STUDY OF THE MARKETABILITY OF ABATEMENT SULFUR PRODUCTS

INTRODUCTION

Our Nation faces a dilemma in implementing the Clean Air Act as amended in 1970, which established strict requirements and timetables for cleaning the air. The dilemma concerns both the direction to take and the achievement of objectives once a direction is determined. Time is critical; the target date of mid-1975 for implementing the SO_x regulations is approaching rapidly.

The solution is far from simple. One major complicating factor is the energy crisis. Supplies of low-sulfur fuels are inadequate for them to be the sole means of achieving compliance. In addition, the design of many electric power plants is not conducive to use of low-sulfur fuel. Other alternatives--such as dispersion techniques, use of products from coal gasification of liquefaction, or addition of flue gas desulfurization systems--must be considered for many plants. Then there is the matter of side effects of SO_x removal systems--e.g., disruption of supply channels for raw materials normally used elsewhere, excessive demand on fabricators of needed equipment, disposal of waste products, and market impact of saleable byproducts.

For the air quality control areas where flue gas desulfurization systems will become the major control technique, numerous alternatives are available as to the type of system to install and the byproducts produced. Byproducts are both waste and saleable material, such as calcium sludge, gypsum, liquid SO_2, ammonium sulfate, elemental sulfur, and various concentrations of sulfuric acid. The large tonnages of these byproducts which could be produced from the SO_2 emissions projected for 1980 could create an overwhelming disposal problem. If all the SO_2 emissions projected for 1980 were converted to saleable materials, the amount of sulfur involved would be about 1.7 times the expected 1980 U.S. consumption of sulfur. On the other hand, if all utilities installed a calcium-based scrubbing throwaway process the impact on the agricultural lime market could be severe. The limestone requirements for this use would be 2.6 times the projected need for agricultural lime. To further complicate this alternative, the resulting calcium sulfate sludge piles in total could exceed the size of the pyramids of Egypt.

In recognition of this dilemma EPA has initiated a research project with TVA to study the possible impacts of saleable abatement materials on existing and future markets. The overall research effort has been arbitrarily divided into five phases.

The proposed fifth phase involves a more detailed market study of the potential utilization of calcium-sulfur sludge by the wallboard manufacturing industry to derive more accurate cost data for comparison of throwaway alternatives. A thorough economic evaluation would be made of the more promising processes--such as the Chiyoda and the carbon absorption plus the oxidation step for conversion of calcium sulfite to sulfate. A preliminary study was conducted early in 1974. At that time a report was prepared by TVA for EPA entitled "Preliminary Feasibility Study of Calcium-Sulfur Sludge Utilization in the Wallboard Industry" by P. A. Corrigan. This report will be discussed later in the paper.

RESULTS OF THE PHASE I STUDY

This study was sponsored by the Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, North Carolina in cooperation with TVA.

The objective was to create a model for estimating the net sales revenue to TVA for marketing the abatement acid which could be produced. The cost of removing sulfur dioxide and producing the sulfuric acid is considered independent from this evaluation.

The study assumes that an acceptable flue gas desulfurization system equipped with a sulfuric acid production process is commercially available and could be installed at TVA steam plants.

Sulfur Dioxide Removal Processes

The sulfur dioxide removal processes being developed with financial assistance from EPA include several which could produce sulfuric acid as a marketable product--the Chemico-basic magnesia scrubbing process, Davy Powergas - Sulfite scrubbing process, and the Monsanto catalytic oxidation process. Philadelphia Electric is installing a privately funded magnesia scrubbing process at its Eddystone plant. The demonstration sized plants in the United States using technology from these processes are listed in Table 1 below:

Table 1. REGENERABLE PROCESS DEMONSTRATION

Process	Demonstration	Utility Company	Product
MgO scrubbing	155 MW oil (1972)	Boston Edison	98% H_2SO_4
	100 MW coal (1974)	Potomac Electric Power	98% H_2SO_4
	120 MW coal (1975)	Philadelphia Electric	98% H_2SO_4
Sodium sulfite scrubbing	115 MW coal (1975)	Northern Indiana Public Service	Sulfur
Catalytic oxidation	110 MW coal (1974)	Illinois Power	80% H_2SO_4

Sulfuric Acid Market

About 90 percent of the elemental sulfur consumed in the United States is used to make sulfuric acid. The following industries use elemental sulfur for non-acid purposes: Agricultural Chemicals, pulp and paper, carbon disulfide, rubber, sugar, starch, malt, and dye stuffs. It is apparent that elemental sulfur and sulfuric acid offer the greatest potential to the electric utilities for abatement production from the SO_2 emissions.

Sulfur dioxide (SO_2) is oxidized by air in the presence of a catalyst to form sulfur trioxide (SO_3) which combines spontaneously and irreversibly with water vapor to form sulfuric acid. There are alternatives as to the source of SO_2 as well as the method of conversion to SO_3.

There are two principal methods for conversion of SO_2 to SO_3 which are known as the chamber and contact processes. The older chamber process, which was introduced in the 18th century, uses nitrogen oxides as an oxygen-carrying catalyst for the conversion of SO_2 to SO_3. The reactions which produce the SO_3 and sulfuric acid take place either in huge lead chambers or packed towers.

The more modern contact process converts SO_2 to SO_3 by use of a metal or metal-oxide catalyst. The SO_3 is then passed through an absorption tower where it is absorbed in recirculating concentrated acid. The major advantages of the contact process are that concentrated acid of high purity can be produced directly and compact plants of high capacity are feasible.

Alternatives sources of SO_2 for manufacture of sulfuric acid include (1) elemental sulfur, (2) pyrites (sulfite ores or iron, copper, lead, or zinc), (3) waste gases from metallurgical refining operations, (4) hydrogen sulfide from sour gas or petroleum, (5) sulfur-bearing ores of volcanic origin, (6) sulfate salts such as gypsum or anhydrite, and (7) waste gases from combustion of sulfur-containing fuels. Only elemental sulfur, pyrites, and sulfates (gypsum) are considered to be true basic raw materials for the production of sulfuric acid since other sources yield SO_2 as a by-product. This study focuses on the potential production of H_2SO_4 from waste gases and combustion of sulfur containing fuels used in electrical generating steam plants.

Current Production

United States production of sulfuric acid in 1972 totaled over 31.1 million short tons (100% H_2SO_4) or about 7.2 percent above 1971's production. This represented approximately 80 percent of the total production capacity in the United States of about 40 million tons. The spacial distribution of the production is approximated in Figure 1. About 60 percent of the production capacity was committed for captive use. Only about 12.5 million short tons was externally marketed from the 1971 production of 29.4 million short tons. The 1970 capacity by states (short tons/day) is outlined in Table 2. The five states having the most capacity for acid manufacture include Florida, Louisiana, Texas, New Jersey, and Illinois.

The size of individual acid plants has increased over the years. Plants of 1,000 tons per day capacity have now become commonplace, and capacity of up to 2,000 tons per day have been recently constructed. Such plants are usually a part of fertilizer complexes. A few of the old chamber process plants are still in operation, but the majority of the plants use the more modern and efficient contact process. Most existing sulfuric acid plants do not have adequate pollution control facilities. This is discussed further in the production-distribution model.

Sulfuric acid is made and used in a variety of concentrations which are usually indicated as follows:

> % H_2SO_4 or °Baume - The simplest description of sulfuric acid concentration is % H_2SO_4. However, because of the distinct relationship between specific gravity and strength (up to 93%) and the simplicity of measuring specific gravity by hydrometer, most acid concentrations up to 93 percent are expressed as degrees Baume. From 93 to 100 percent acids are referred to by % concentration of H_2SO_4.

Current Consumption

The major end uses of sulfuric acid in the United States in 1970 are shown in Table 3. Fertilizer consumption represented 54 percent of the sulfuric acid consumed. The long-range growth in acid consumption is estimated to be about 4 to 6 percent per year which is closely tied to the fertilizer growth pattern.

Although most sulfuric acid consumed in fertilizer manufacture is a concentrated, high-quality material, off-grade acid could be used as well. For other end uses of sulfuric acid, high purity and high concentration are almost mandatory.

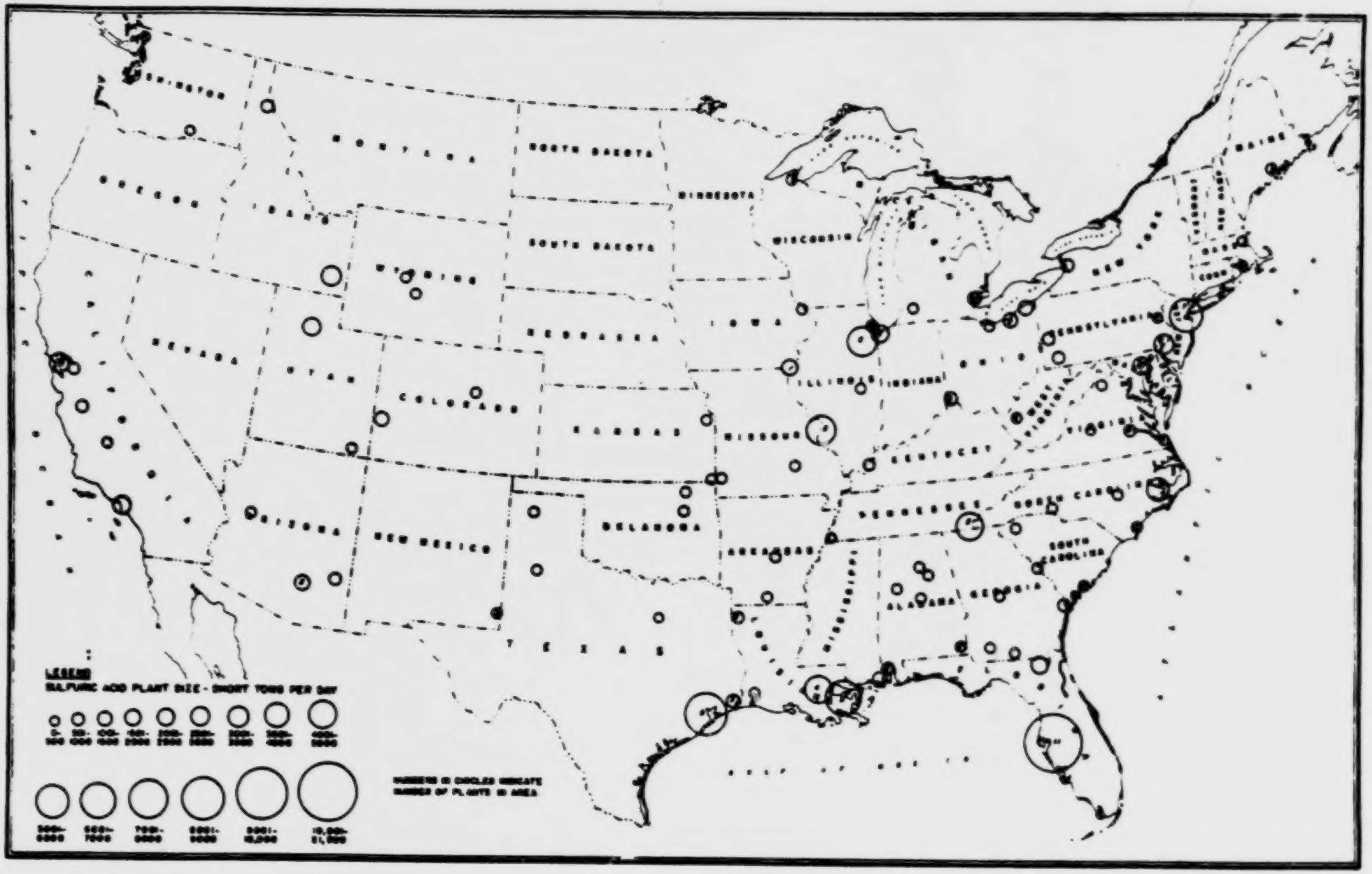
LEGEND
SULFURIC ACID PLANT SIZE - SHORT TONS PER DAY
NUMBERS IN CIRCLES INDICATE NUMBER OF PLANTS IN AREA
MONTANA
SOUTH DAKOTA
MINNESOTA
WISCONSIN
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
NEW MEXICO
COLORADO
SOUTH CAROLINA

Figure 1. Sulfuric acid manufacturing capacity (1970).

Table 2. SULFURIC ACID PLANT CAPACITY (1970)
(short tons/day)

State	Capacity	State	Capacity
Alabama	1,610	Mississippi	1,067
Arizona	2,627	Missouri	3,303
Arkansas	737	New Jersey	6,913
California	6,774	New Mexico	446
Colorado	1,483	New York	583
Delaware	1,050	North Carolina	3,480
Florida	23,661	Ohio	3,180
Georgia	1,369	Oklahoma	630
Idaho	3,470	Pennsylvania	2,177
Illinois	6,944	Rhode Island	50
Indiana	2,066	South Carolina	324
Iowa	1,877	Tennessee	4,421
Kansas	747	Texas	9,855
Kentucky	550	Utah	2,133
Louisiana	12,600	Virginia	1,983
Maine	223	Washington	333
Maryland	2,260	West Virginia	470
Massachusetts	330	Wisconsin	67
Michigan	1,301	Wyoming	360
Grand Total	113,454		

Table 3. SULFURIC ACID END USE PATTERN (1970)

End Uses	Thousand short tons (100% basis)
Fertilizer	
Phosphoric acid products	13,750
Normal superphosphate	1,240
Cellulosics	
Rayon	520
Cellophane	170
Pulp and paper	600
Petroleum alkylation	2,400
Iron and steel pickling	800
Nonferrous metallurgy	
Uranium ore processing	300
Copper leaching	350
Chemicals	
Ammonium sulfate	
Coke oven	500
Synthetic	480
Chemical by-product	190
Chlorine drying	150
Alum	600
Caprolactam	260
Dyes and intermediates	370
Detergents, synthetic	400
Chrome chemicals	100
HCl	150
HF	880
TiO_2	1,440
Alcohols	1,800
Other chemicals	380
Industrial water treatment	200
Storage batteries	140
Other processing	470
Total	28,640

It is apparent from Table 3 that sulfuric acid has a wide variety of uses. Some uses are based on excellent physical qualities, but cost is also important. Sulfuric acid is often preferred over other mineral acids, chemicals, or different process technology because it is the least expensive. For example, in phosphate rock acidulation and phosphoric acid manufacture, it is the lowest cost acidulant available. Also, the use of sulfuric acid for leaching low-grade copper oxide ores has been feasible only because of the availability of low-cost byproduct sulfuric acid from western copper smelting operations.

Current Transportation

Location of power plants equipped with sulfur dioxide removal and sulfuric acid production facilities will have a major influence on the marketing costs of abatement acid production. That is, power plants that enjoy the use of water transportation will be in a position to reach more distant markets due to the relatively lower transportation costs as compared to rail or truck. Figure 2 outlines the relative costs of shipping sulfuric acid by barge, rail, and truck. (P. 44, Sulfur Markets for Ohio Utilities, by J. F. Foster, et. al., EPA 450-3-74-026).

Sulfuric Acid Production Capacity of TVA

TVA is a corporate agency of the United States created by the Tennessee Valley Authority Act of 1933. In addition to various other programs, TVA operates a system supplying the power requirements for an area of approximately 80,000 square miles containing about 6 million people. Except for direct service by TVA to certain industrial customers and Federal installations with large or unusual power requirements, TVA power is supplied to the ultimate consumer by 160 municipalities and rural electric cooperatives which purchase their power from TVA. TVA is interconnected at 26 points with neighboring utility systems.

Power loads on the TVA system have doubled in the past 10 years and are expected to continue to increase in the future. To keep pace with the growing demand it has been necessary to add substantial capacity to the generating and transmission system on a regular basis. Current plans are based on meeting future additional requirements with nuclear power stations.

The following tabulation breaks down the TVA power generating system capacity into several categories:

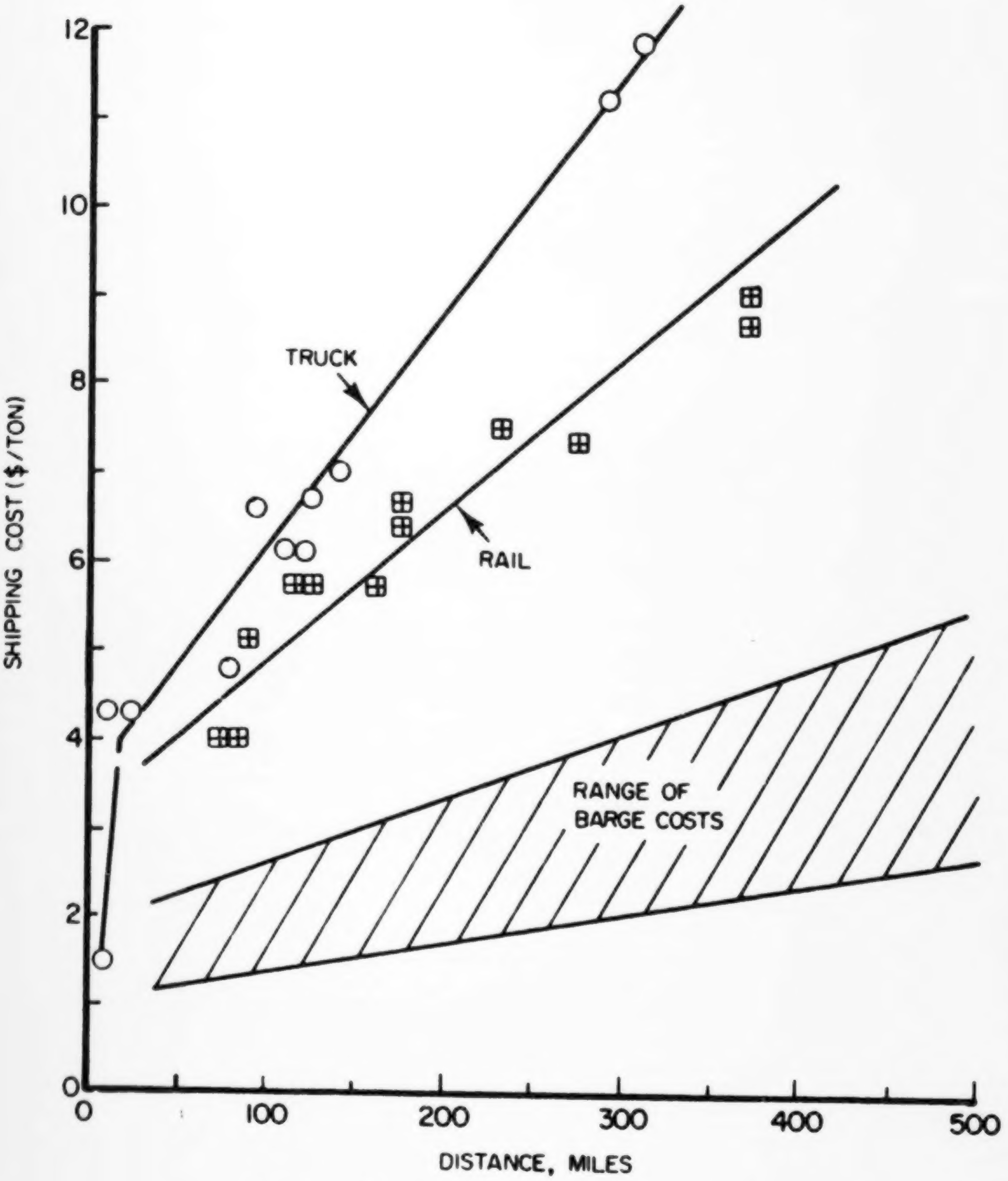

Figure 2. Sulfuric acid shipping cost.

	Capacity in service June 30, 1972		Under Construction or scheduled	
	No. of plants	Megawatts	No. of plants	Megawatts
Coal-fired steam plants	11	15,509	1	2,600
Hydroelectric plants	29	3,185		
Nuclear plants			4	11,101
Gas-or-oil-fired turbines	2	688		

Figure 3 shows the location of TVA's present generating facilities and those under construction.

The total of 18,109 megawatts of coal-fired capacity is of primary interest because it represents the potential for sulfuric acid production. However, only a portion of this capacity is used as "base load"--that is, operated continuously except for maintenance. These are the newer, larger and more efficient plants. The other portion is used as "swing load," that is, intermittently, or at times of peak demand. These are the older, smaller and less efficient plants.

The TVA plants which would have the greatest potential for the installation of sulfuric acid production facilities would be the base-load coal-fired plants, except Bull Run which burns low-sulfur-content coal, 1.5 percent. This is based on the indication that SO_2 recovery and sulfuric acid-producing facilities would be less competitive in intermittent service for TVA than limestone scrubbing or other "throwaway processes" facilities. Also, SO_2 recovery and acid-producing facilities operate more efficiently under continuous duty with constant operating conditions.

One of the relatively new and large units is being equipped with a limestone scrubbing SO_2 removal system. This plant is the Widows Creek Unit 8 and is not considered a potential sulfuric acid producer. The swing load plants -- Colbert Units 1-4, John Sevier, Johnsonville 1-6, and Kingston -- generally would have limited potential for acid production.

Therefore, of the total 18,109 megawatts of coal-fired capacity, 9,806 megawatts would be considered for sulfuric acid production.

To determine the amount of acid which could be produced by the 9,806 megawatts, it was assumed that about 90 percent of the sulfur in the coal would end up as SO_2 in the stack gas. The remaining sulfur is rejected in the coal mills as pyrites, left in

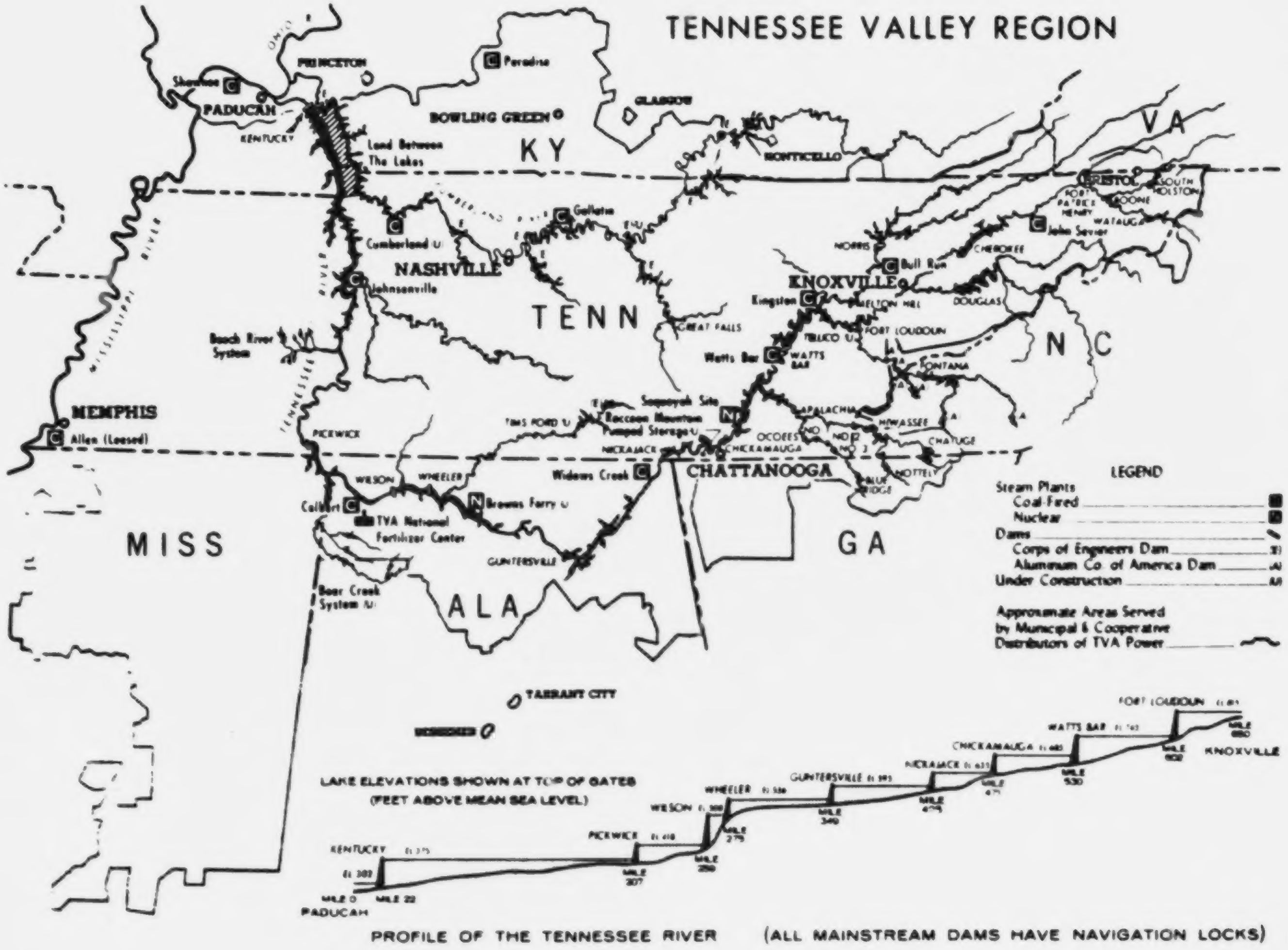
TENNESSEE VALLEY REGION
KY
TENN
MISS
ALA
GA
N C
VA
PADUCAH
Shawnee
PRINCETON
Paradise
BOWLING GREEN
GLASGOW
MONTICELLO
Land Between The Lakes
KENTUCKY
Cumberland
Gallatin
NASHVILLE
Johnsonville
Beech River System
MEMPHIS
Allen (Leased)
PICKWICK
WILSON
WHEELER
Colbert
TVA National Fertilizer Center
Browns Ferry
GUNTERSVILLE
Bear Creek System
Widows Creek
Sequoyah Site
Raccoon Mountain Pumped Storage
TIMS FORD
NICKAJACK
CHICKAMAUGA
CHATTANOOGA
OCOEES
APALACHIA
HIWASSEE
CHATUGE
NOTTELY
BLUE RIDGE
FONTANA
Watts Bar
WATTS BAR
TELLICO
FORT LOUDOUN
MELTON HILL
Kingston
KNOXVILLE
NORRIS
Bull Run
DOUGLAS
CHEROKEE
John Sevier
WATAUGA
BOONE
FORT PATRICK HENRY
SOUTH HOLSTON
BRISTOL
GREAT FALLS
TARRANT CITY
LEGEND
Steam Plants
Coal-Fired
Nuclear
Dams
Corps of Engineers Dam
Aluminum Co. of America Dam
Under Construction
Approximate Areas Served by Municipal & Cooperative Distributors of TVA Power
LAKE ELEVATIONS SHOWN AT TOP OF GATES (FEET ABOVE MEAN SEA LEVEL)
KENTUCKY
PICKWICK
WILSON
WHEELER
GUNTERSVILLE
NICKAJACK
CHICKAMAUGA
WATTS BAR
FORT LOUDOUN
MILE 0
MILE 22
MILE 207
MILE 259
MILE 275
MILE 349
MILE 425
MILE 471
MILE 530
MILE 602
MILE 650
PADUCAH
KNOXVILLE
PROFILE OF THE TENNESSEE RIVER (ALL MAINSTREAM DAMS HAVE NAVIGATION LOCKS)

Figure 3. Location of TVA power plants.

the ash, or unaccounted for. For every pound of sulfur oxidized, 2 pounds of SO_2 are produced and for every pound of SO_2 that is recovered, 1.53 pounds of sulfuric acid can be produced. Furthermore, it was also assumed that the SO_2 removed for each plant would be based on the EPA emission standard for new coal-fired steam plants--1.2 pounds of SO_2 per million Btu heat input.

Using these assumptions, plus projections for sulfur in coal and the amount of generation expected at each plant (supplied by TVA Division of Power Resource Planning), estimates of potential sulfuric acid production from TVA's plants from 1975 through 1985 were made. Consideration was given to the oncoming new plants -- coal-fired and nuclear -- and the effect of time, age, and maintenance on operating schedules for existing plants. Coal analyses were based on 1972 data. It would, of course, be impossible for acid facilities to be installed by 1975; however, this is the base year assumed for startup. The forecast is as follows:

Forecasted Theoretical Production of Sulfuric Acid

(M Tons)

Steam plant and unit	1975	1977	1980	1983	1985
Colbert 5	121.9	121.9	121.9	84.4	84.4
Cumberland 1-2	578.7	578.7	578.7	520.8	471.2
Gallatin 1-4	165.3	159.8	137.8	99.2	71.6
Johnsonville 7-10	135.9	135.9	111.9	55.9	40.0
Paradise 1-3	617.3	617.3	608.4	573.2	546.7
Shawnee 1-10	270.0	253.5	253.5	137.8	99.2
Widows Creek 7	92.6	92.6	86.0	66.1	52.9
TOTAL	1,981.7	1,959.7	1,898.2	1,537.4	1,366.0

Market Approach

The major sulfuric acid manufacturing-marketing schemes which prevail in the existing market are:

1. Production of acid near the point of use from purchased sulfur.

2. Production of acid near the source of sulfur by the basic sulfur producer.

3. Marketing of spent or regenerated acid.

4. Marketing of acid recovered from pollution abatement processes.

The first (production from purchased sulfur) is the most vulnerable because the producer is dependent on an external source of sulfur. The acid producer who is basic in sulfur in No. 2, above, would consider the investment in mining facilities as a sunken investment. This means that he would take into account only his out-of-pocket costs in meeting market price pressures from abatement sulfur products. The arrangements for utilization of spent acids (No. 3, above) are highly specialized. It would, therefore, be difficult to place abatement acid in the regenerative acid market.

The most orderly way to incorporate the abatement acid into the existing market would be to replace the capacity of sulfur-burning sulfuric acid plants. Such plants purchase sulfur from external sources. Therefore, the marketing strategy assumed for this study is to substitute abatement acid for purchased sulfur.

Market Potential for abatement acid

TVA's National Fertilizer Development Center maintains a computerized file of world-wide manufacturers of fertilizers and related products. A list of sulfur-burning acid plants currently in production or planned thru 1975 was developed from the TVA file. The potential market was limited to a 10-state area on the inland-waterway system in the central United States. All the TVA power plants are located with access to this waterway. The states selected included: Alabama, Arkansas, Illinois, Kentucky, Louisiana, Mississippi, Missouri, Ohio, Tennessee, and Texas. Florida was included as an alternate marketing area if required.

Information from the TVA file offered the following data for sulfuric acid plants:

1. Company
2. Location
3. Annual capacity
4. Type of process

Dates of construction and major capital improvements were obtained from other sources. A total of 61 sulfuric acid plants were selected as potential points for acid sales. These points can be grouped into seven metropolitan market areas -- Memphis, Houston, Chicago, New Orleans, Cincinnati, Columbus, and Tampa.

The production from the 61 plants represents the market potential for abatement acid. The market demand from these plants is dependent upon price incentive. The primary incentive to purchase acid will be the cost reduction enjoyed as compared to manufacturing the acid from purchased sulfur. This assumes that price, quality, and convenience are the major factors that influence product or process substitution. It is further assumed that the acid plant will buy abatement acid if the delivered cost is lower than its production cost. The more inefficient plants become the prime consumer of abatement acid. In order to move the total production, some of the more efficient plants would have to be shut down; therefore, the price will be influenced by the volume of abatement production.

Avoidable Costs

Avoidable costs are defined as those costs which a producer would not incur if he discontinued the operation of his plant. They are:

Cost Category	Cost Breakdown
Raw material	Sulfur
Utilities	Electric power, cooling water, process water, boiler-feed water.
Operating Expenses	Labor, supervision, payroll overhead.
Capital Costs	Amortized costs for maintenance of existing facilities plus amortized costs of new capital investment at the end of useful plant life.

An adjustment for loss of steam generation in the acid plant is required.

Sulfuric Acid Production - Distribution Model

In the derivation of a model to maximize the net sales revenue from the sale of abatement acid the following factors were considered:

1. Trade off between avoidable costs at 61 acid plants and shipping distances from seven power

plants.

2. Effect of sulfur price.

3. Effect of volume on net sales revenue.

The combinations of these factors contribute to the complexity of the evaluation; therefore, use of a computer is almost essential to establish maximum revenues. A production-distribution model (similar to a transportation linear program model) was developed to handle the several variables. The objective of the model is to minimize acid costs to the existing sulfuric acid plant locations while maximizing net sales revenue to TVA.

The programming model was designed so that the key technical and economic parameters can be varied. Table 4 lists the major parameters and shows typical values.

The first three parameters relate to sulfur conversion efficiency as a function of plant design; the data are based on a report by the Chemical Construction Corporation. Plants built prior to 1960 average 95.5 percent conversion. The newer plants are more efficient, 97 percent. Parameters 4 thru 9 are used to calculate the manufacturing costs of sulfuric acid. (An example is shown in Table 5). The values for the investment parameters 4 thru 6 are estimates based on the initial capital estimates shown in Table 5. The utility costs (parameter 7) are fixed per ton of sulfuric acid and the operating expenses (parameter 8) are annualized; taxes and insurance (parameter 9) are proportional to initial capital investment.

The annual costs are calculated in perpetuity utilizing the discounted cash flow analysis method. The outlay streams are then amortized, or averaged over all years in the firms planning horizon. The cost streams are composed of (1) constant annual expenditures for sulfur, utilities, and operating expenses; (2) periodic expenditures for new plants; and (3) maintenance of existing facilities which is assumed to grow at a compound rate. The impact of inflation is not included in the analysis. These cost streams are presented in Figure 4. It is noted that the average capital costs decline as useful life increases.

The optimium useful life is identified as the minimum point on the average total cost curve. At this point the added capital cost savings enjoyed by increasing useful life one year equals the added maintenance saving from shortening useful life one year. It is noted that the average total cost curve in Figure 4 is very flat over a wide range of years. The average capital charge of 14.9 percent, which is identified in Table 5, covers a range from 29 to 41 years. Possibly random effects, such as

Table 4. MAJOR PARAMETERS IN MODEL

No.	Description of variable	Example value	Fortran name
1	Tons of sulfur per ton H_2SO_4 (before YEAR60)	.3053	PRE60
2	Tons of sulfur per ton H_2SO_4 (after YEAR60)	.3006	POST60
3	Year of technology change	60.	YEAR60
4	Sulfuric acid plant investment ($/ton-year)	27.285	EXPENDO
5	Capacity for this plant (M tons/year)	247.5	SIZE0
6	Scale factor for determining investment for other sized plants	.734054	FACTOR
7	Fixed conversion cost per ton ($/ton)	.47	AVC
8	Fixed annual conversion cost ($/year)	116.620	AFC
9	Taxes and insurance rate	.015	TIR
10	Time preference rate for money	.08	RATEI
11	Compound maintenance rate	.04	RATEM
12	Economic useful life	34.	USELIFE
13	Percent H_2SO_4 concentration	98.	ACDCON
14	Port Sulphur price ($/short ton)	22.32	PS
15	TVA H_2SO_4 price ($/ton H_2SO_4)	0.	PA
16	Proportion of 330 TPD capacity estimate	1.	DEMAND
17	Number of steam plants	7.	NPLANTS
18	Number of acid plants	61.	JNUM
19	Number of years considered	1.	NYEARS
20	Years considered	75.	YEAR(1)

Table 5. PRODUCTION COST ESTIMATES FOR SULFURIC ACID

Acid plant	Capacity			
Tons per day	50	250	750	1,500
Tons per year, at 330 days/yr	16,500	82,500	247,500	495,000
Initial capital, $	909,000	3,090,000	6,907,000	10,905,000
Unit capital, $/ton-yr	55.09	37.45	27.91	22.03
Operating costs, $				
Utility costs				
Electric power	11,570	57,800	172,700	346,600
Cooling water	6,040	30,200	90,300	181,200
Process water	70	350	1,020	2,100
Boiler feed water	980	4,910	14,730	29,440
Steam (credit)	-10,870	-54,400	-163,000	-326,000
Labor				
Operating	47,500	47,500	47,500	47,500
Supervision	21,100	21,100	21,100	21,100
Overhead at 70% above	48,020	48,020	48,020	48,020
Capital costs, $				
Amortized value of maintenance plus capital outlays at optimal useful life (29-41 yr), 14.9%	135,441	460,410	1,029,143	1,624,845
Taxes and insurance, 1-1/2%	13,635	46,350	103,605	163,575
Annual operating cost, $ (excluding sulfur)	273,486	662,240	1,365,118	2,138,380
Unit cost, $/ton (excluding sulfur)	16.57	8.03	5.52	4.32

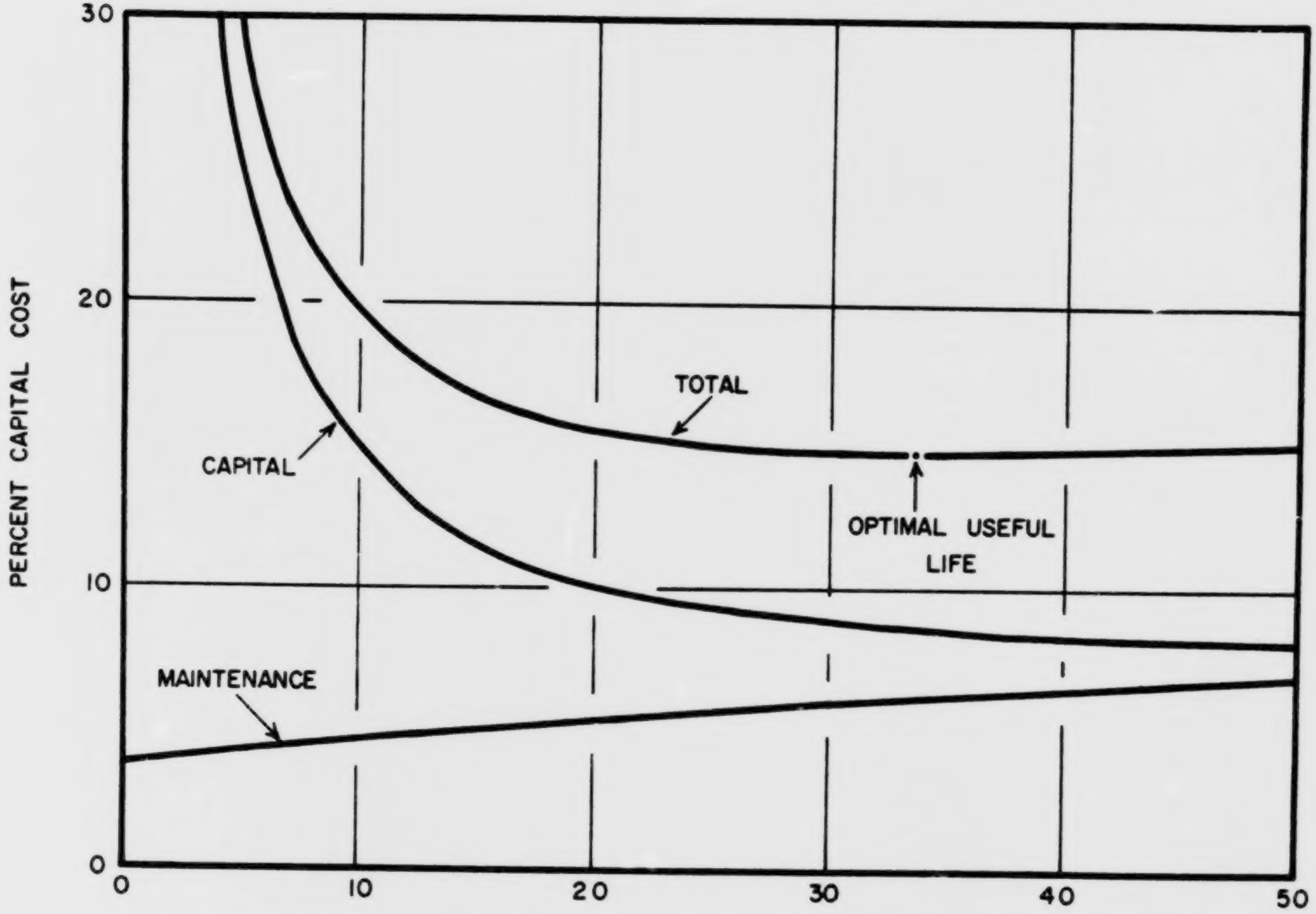

Figure 4. Amortized value of maintenance and capital outlays for new plants. (Assuming 8% interest and 4% compound maintenance).

abrupt physical, economic, technological, or environmental changes play the dominant role during this period with regards to the timing of plant replacement.

The unique concept incorporated into this model relates to the method used for handling existing plants as compared to the traditional static analysis used to justify the investment in a new plant. For existing plants, the initial capital expenditures represent a "sunken investment," and, therefore, do not enter directly into the firm's decision-making process for making the decision to discontinue present production and buy abatement sulfuric acid. Only avoidable costs are considered in making this decision.

It can be demonstrated that only when avoidable costs are considered for a one-year-old plant the level of costs decrease from 14.9 percent of the initial investment to 7.1 percent. At this point, the added savings from postponing the building of a new plant is just offset by added maintenance costs in the 34th year which is exactly equal to the optimal useful life for a new plant.

When the model is focused on a thirty-year-old plant it is noted that the level of costs have risen to 14.6 percent of the initial capital expenditure and the optimal useful life is still 34 years. It is recognized that management of a new plant is not concerned with replacement alternatives, but the management of an old plant is faced with impending replacement alternatives.

The managers handling the older plants should be receptive to exploring the alternative of purchasing abatement acid because their maintenance costs are high and within a few years they will be faced with the imminent decision of plant modernization.

The computer program calculates the above mentioned costs based on (1) an interest rate of 8 percent of total investment (parameter 10, Table 4); (2) a maintenance rate of 4 percent of the initial investment compounded annually at the rate of 4 percent (parameter 11, Table 4); and (3) plant age. The user is given the freedom of selecting useful life (parameter 12, Table 4). The program can be modified to calculate and use the optimum value for this parameter.

Parameters 13 thru 20, Table 4, relate to the logistical portion of the model. It is assumed that the competitive pricing structure for sulfur in the United States is based on a Gulf Coast price plus transportation costs to a given sulfur-burning sulfuric acid plant. This assumption seems reasonable since firms buying imported sulfur continually bargain against Gulf Coast producers.

The model allows each acid plant three choices: (1) continue to operate existing plant; (2) rebuild and operate a new plant; and (3) shut down existing plant and buy acid. The abatement acid would be expected to enter the market at a price no higher than the cost which could be avoided by shutting down the most inefficient plant. The actual price of the abatement acid is influenced by the volume offered in the market. The model selects the most profitable choice for the acid plant by minimizing acid costs at existing sulfuric acid plant locations.

The solution to the model ranks all acid producers in terms of production costs, age, size, and relative location from their sulfur source as well as the abatement acid source. The plants with the highest production costs become the prime consumers of the abatement acid. This group has the oldest plants with the lowest production capacity located in the more remote areas from the Gulf Coast sulfur producer.

The FOB abatement acid price (initially zero) plus fixed handling cost per ton associated with each steam plant are added to the transportation costs in order to determine the delivered price to each sulfuric acid plant. The maximum net sales revenue is derived by adjusting the FOB price of the acid until the total volume is sold. It is maximized by realizing the trade-off between avoidable production costs at 61 acid plants and the shipping distances from seven power plants.

Another important economic factor is the cost of pollution abatement facilities that must be added to existing sulfur-burning acid plants. This cost could be expected to vary considerably from one plant to another due to age of plant and process used. Based on Chemical Construction Corporation data, it is assumed that the average would be about $3 per ton. This factor is not included in the program; and in many cases, net revenue results shown later in the report could be increased by this amount.

The program is written so that one or more years can be considered simultaneously for a given run. The model examines each plant to determine if that firm would be better off continuing production or buying abatement acid. It also determines the optimum distribution pattern from each steam plant to each acid plant. This optimization is done in such manner as to result in the lowest possible industry cost. The model can determine the quantity of acid sold at a given price or the highest price which will just move the required amount for each steam plant.

The model is written for Control Data Corporation Kronos time-sharing and can run from most any location through a standard telephone. Furthermore, the program can be made available to anyone interested in its use. The heart of the model is a conversational linear programming package called APEX. The present program calculates cost of each acid plant-steam plant combination (presently over 400) and then generates the required input data file. APEX is run to optimize the model and a second program interprets solutions as printed reports. An interactive system is also available which can display any or all of the standard linear programming solution values.

Freight Rates and Handling Charges

Freight rates used in the model were obtained from TVA's Navigation Economics Branch which is located in Knoxville, Tennessee. These rates can be divided into two categories:

1. Those used for shipping sulfur from Port Sulfur, Louisiana to various plant locations. These rates were used as a factor in determining the costs of sulfuric acid production of each plant location.

2. Those rates for shipping sulfuric acid from the seven TVA steam plants to each of the sulfuric acid production locations. These rates are a factor in determining the net back to TVA.

An estimated cost of 20 cents per ton has been programmed into the model to cover acid storage at the existing acid plants. This would provide 30-day storage. The storage cost is based on an estimated capital cost for the tanks and the auxiliary facilities at $20 per ton.

Results of the Study

The base case market pattern is shown in Table 6 as the most economical market pattern for TVA abatement acid given the assumptions outlined in this study. The maximum net sales revenue, excluding production cost, is identified as $8.76 per ton which is the lowest of the marginal costs shown for each of the seven steam plants. In this case, acid would be shipped by barge from seven production points (steam plants) to 20 marketing points (sulfuric acid plants). If a credit is added for the estimated increased cost for installation and operation of tail gas clean-up system on existing acid plants the net sales revenue would increase by approximately $3 per ton of acid or a total of $11.76.

The effect that a change in TVA's net sales revenue or "price" has on acid sales is shown in Figure 5 for the base case.

Table 6. BASE CASE MARKET PATTERN FOR TVA H_2SO_4

(M TONS)

SULFUR PRICE = $22.32 ACID CONCENTRATION = 98% CAPACITY = 100% BARGE = 100%

MAXIMUM TVA ACID PRICE WOULD BE $ 8.76

PLANT LOCATION	PRODUCTION CAPACITY	ACTUAL PROD'N	YEAR BUILT	SULFUR REDUC'N ($)	STEAM PLANT SALES COLB	CUMB	GALL	PARA	SHAW	WIDC	JOHN
2. N.LITTLE ROCK,AR	86	0	46	7.25	0	0	0	0	0	86	0
28. E.ST.LOUIS,ILL.	153	0	37	7.38	92	0	0	55	0	7	0
29. MONSANTO,ILL	139	0	67	1.40	0	0	0	139	0	0	0
30. E.ST.LOUIS,ILL.	239	0	54	2.50	0	0	0	239	0	0	0
32. CALUMET CITY,ILL	111	0	56	3.87	0	35	0	76	0	0	0
33. JOLIET,ILLINOIS	36	0	54	17.06	0	0	36	0	0	0	0
35. JOLIET,ILLINOIS	256	0	45	1.24	0	127	129	0	0	0	0
36. STREATOR,ILL.	35	0	51	13.91	0	35	0	0	0	0	0
37. E.CHICAGO,IND.	334	72	37	0.	0	18	0	0	108	0	136
38. LASALLE,ILLINOIS	35	0	37	21.89	0	35	0	0	0	0	0
40. JOLIET,ILLINOIS	299	0	42	.68	0	299	0	0	0	0	0
41. CALUMET CITY,ILL	30	0	47	22.90	30	0	0	0	0	0	0
42. CHICAGO HTS,ILL	30	0	60	17.39	0	30	0	0	0	0	0
46. BATON ROUGE,LA.	90	0	53	0.	0	0	0	0	90	0	0
47. NEW ORLEANS,LA.	30	0	65	8.56	0	0	0	0	30	0	0
54. HAMILTON,OHIO	63	0	48	11.35	0	0	0	63	0	0	0
55. CINCINNATI,OHIO	30	0	46	28.03	0	0	0	30	0	0	0
56. CINCINNATI,OHIO	16	0	38	44.54	0	0	0	16	0	0	0
60. COLUMBUS,OHIO	18	0	37	22.54	0	0	0	0	18	0	0
61. COLUMBUS,OHIO	24	0	37	15.07	0	0	0	0	24	0	0
PLANT CAPACITY					122	579	165	617	270	93	136
PLANT PRODUCTION					122	579	165	617	270	93	136
MARGINAL ACID COST ($)					9.27	9.78	9.27	9.27	10.19	8.76	9.78

TOTAL PRODUCTION = 1982

TOTAL NET SALES REVENUE = $ 17351886

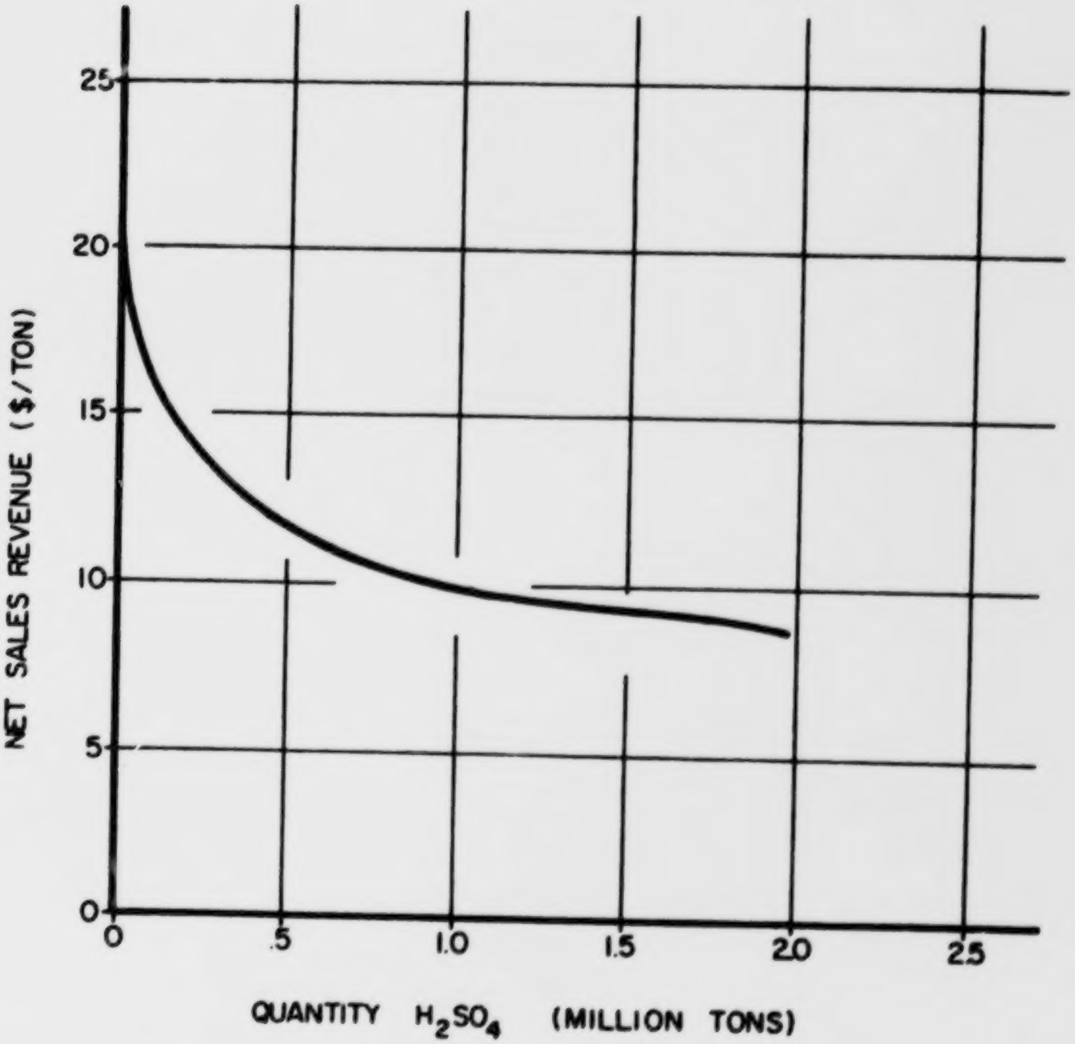

Figure 5. Demand for TVA sulfuric acid.

As expected, acid movement declines as the "price" of TVA acid increases. In order to move all of its acid, TVA could charge no more than $8.76 per ton plus freight. It could expect to move only about one-half of its production for $10. At $20 per ton of acid, no acid could be sold externally.

By adjusting the assumptions in the model from 100 percent barge transportation to a mixed rail and barge coupled by a reduction in market demand equivalent to 75 percent of on-stream time for existing acid plants the net sales revenue is reduced to $5.99 per ton without credit for tail gas clean-up at the acid plant. The results are outlined in Table 7.

The revenue from the sale of abatement acid given the assumptions used in this study is directly proportional to the sulfur price. That is, the increase of $5 per long ton of sulfur is equivalent to approximately $1.42 increase in potential net sales revenue for abatement acid. (Figure 6) The shipment of 80 percent acid instead of 98 percent acid increased the transportation and handling costs by $1.00 per ton of acid which reduces the net revenue in the same amount.

Another consideration in the study which has wide implications involves the use of the abatement acid internally to produce a more valuable phosphoric acid for fertilizer production. Table 8 outlines the production costs for a phosphoric acid plant which would utilize the abatement sulfuric acid production which could be produced from both Colbert #5 (550 MW) and Widow's Creek #7 (575 MW) or a total of 221,000 tons of sulfuric acid. A phosphoric acid plant sized to use this amount of sulfuric acid would produce about 74,250 tons of P_2O_5 per year. This would allow TVA to enjoy the savings incurred by producing its own P_2O_5 in lieu of purchasing P_2O_5 and at the same time enjoy an increase in net sales revenue in the amount of 51 cents a ton for abatement sulfuric acid.

The study indicates that the most orderly way to incorporate the abatement acid into the market would be to replace sulfuric acid currently produced from purchased sulfur. The potential sulfuric acid production from the TVA system could be incorporated gradually into the market as long as there was no significant competition from other abatement sources. The resulting net sales revenue could reduce the cost of operating the sulfur dioxide control system by an estimated 10 to 20 percent.

Perhaps the most important result from the study is the development of a practical versatile computer program which can be used to extend the market investigation of abatement acid production to the entire United States. Also, the initiation of a data file on

Table 7. MOST LIKELY MARKET PATTERN FOR TVA H_2SO_4

(M TONS)

SULFUR PRICE = $22.32 ACID CONCENTRATION = 98% CAPACITY = 75% BARGE = 80%

MAXIMUM TVA ACID PRICE WOULD BE $ 5.99

PLANT LOCATION	PRODUCTION CAPACITY	ACTUAL PROD'N	YEAR BUILT	SULFUR REDUC'N ($)	STEAM PLANT SALES						
					COLB	CUMB	GALL	PARA	SHAW	WIDC	JOHN
1. HELENA,ARK.	101	0	67	7.52	101	0	0	0	0	0	0
2. N.LITTLE ROCK,AR	64	0	46	15.19	0	0	0	0	0	0	64
28. E.ST.LOUIS,ILL.	115	0	37	14.64	0	0	10	35	0	70	0
29. MONSANTO,ILL	104	0	67	8.37	0	0	0	104	0	0	0
30. E.ST.LOUIS,ILL.	179	0	54	9.13	0	0	0	179	0	0	0
31. MARSEILLES,ILL.	157	0	62	1.62	0	0	0	0	157	0	0
32. CALUMET CITY,ILL	83	0	56	7.91	0	0	0	83	0	0	0
33. JOLIET,ILLINOIS	27	0	54	23.92	0	0	0	27	0	0	0
35. JOLIET,ILLINOIS	192	0	45	4.53	0	192	0	0	0	0	0
36. STREATOR,ILL.	26	0	51	22.74	0	0	0	0	26	0	0
37. E.CHICAGO,IND.	250	0	37	0.	0	190	0	0	60	0	0
38. LASALLE,ILLINOIS	26	0	37	29.41	0	0	0	0	26	0	0
40. JOLIET,ILLINOIS	224	0	42	3.88	0	117	0	107	0	0	0
41. CALUMET CITY,ILL	22	0	47	30.81	0	22	0	0	0	0	0
42. CHICAGO HTS,ILL	22	0	60	24.91	0	22	0	0	0	0	0
46. BATON ROUGE,LA.	67	0	53	7.79	21	34	0	0	0	0	13
47. NEW ORLEANS,LA.	22	0	65	19.49	0	0	0	0	0	22	0
52. GEISMAR,LA.	58	0	68	3.42	0	0	0	0	0	0	58
54. HAMILTON,OHIO	47	0	48	21.22	0	0	0	47	0	0	0
55. CINCINNATI,OHIO	22	0	46	39.16	0	0	0	22	0	0	0
56. CINCINNATI,OHIO	12	0	38	59.82	0	0	0	12	0	0	0
57. COLUMBUS,OHIO	48	4	65	0.	0	0	44	0	0	0	0
58. COLUMBUS,OHIO	40	0	49	9.35	0	0	40	0	0	0	0
59. COLUMBUS,OHIO	40	0	55	0.	0	0	40	0	0	0	0
60. COLUMBUS,OHIO	13	0	37	37.49	0	0	13	0	0	0	0
61. COLUMBUS,OHIO	18	0	37	28.09	0	0	18	0	0	0	0
PLANT CAPACITY					122	579	165	617	270	93	136
PLANT PRODUCTION					122	579	165	617	270	93	136
MARGINAL ACID COST ($)					6.65	6.97	6.62	6.84	7.57	5.99	7.01

TOTAL PRODUCTION = 1982 TOTAL NET SALES REVENUE = $ 11872170

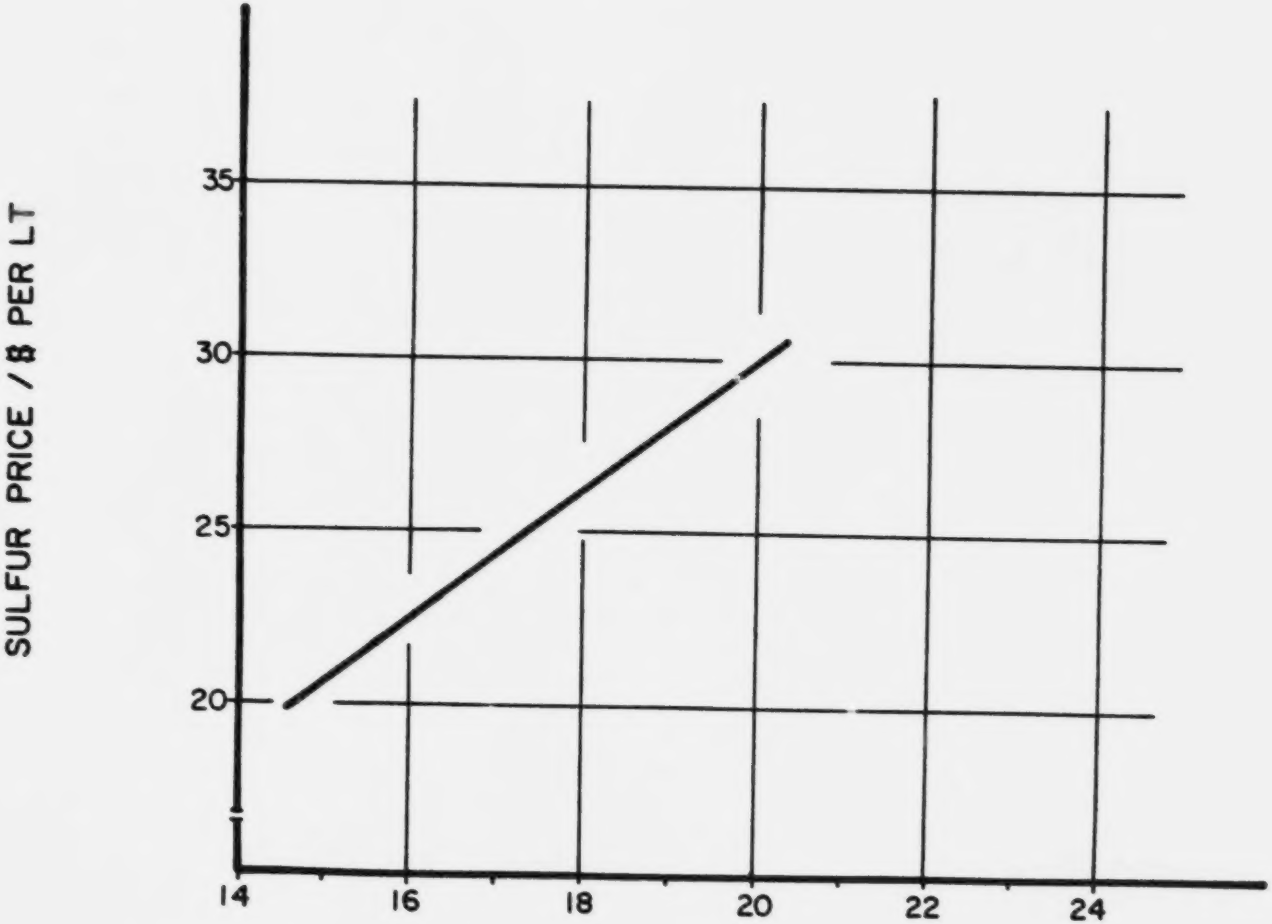

Figure 6. Effect of sulfur price on TVA net sales revenue.

Table 8. PRODUCTION COSTS FOR PHOSPHORIC ACID PLANT

(225 tons/day)

Annual Operating Costs	\$/Ton P_2O_5
Direct cost	
Phosphate rock, 31.1% P_2O_5 (68% BPL) 3.58 tons at \$14.25/ton	51.00
Sulfuric acid, transportation cost from Colbert and Widows Creek, 2.7 tons at \$1/ton (truck rate)	2.70
Labor, 0.83 man-hr at \$6.50	5.40
Maintenance, 6% of plant cost	7.20
Electricity, 330 kWh, \$0.006/kWh	1.98
Cooling water, 5.5 M gal at \$0.02/M gal	0.11
Supplies, analysis, and handling	2.20
Total direct cost	70.59
Indirect cost	
Insurance and taxes, 2% of plant cost	2.40
Depreciation, 12 yr	10.00
Overhead, 100% labor	5.40
Interest, 7-1/2%	4.50
Total indirect cost	20.22
Total production cost	90.81[a]

[a] This is equivalent to \$0.91/unit of P_2O_5 (unit = 20 lb). The net savings would be about \$1.25 minus \$0.91 equals \$0.34/unit of P_2O_5 or

\$34 per ton of P_2O_5

\$2,524,000 per year

sulfuric acid, sulfur sources, and end use patterns is in the development stage. Both the data file and the computer program can be made available to other interested users.

PRELIMINARY FEASIBILITY STUDY OF CALCIUM-SULFUR SLUDGE UTILIZATION IN THE WALLBOARD INDUSTRY

Several sulfur dioxide removal systems under development are based on discarding the sulfur in the form of waste calcium solids; however, there are many steam-electric generating plants, especially in the East, which do not have the necessary land area for such disposal. Therefore, an interest has developed toward conversion of these "throwaway" materials to useful products.

One such possibility is the use of the calcium-sulfur sludge to replace mined, native gypsum in wallboard manufacture. In 1972, U.S. gypsum producers mined 12,328,000 tons while 7,718,000 tons were imported. Because of the low cost of water transportation most imported material was shipped by water to users on the Atlantic, Pacific, and Gulf Coasts. In the same year, 20,076,865 tons of gypsum was used in the United States and 14,205,069 tons of this, or 71 percent, was used in wallboard manufacture. Altogether, gypsum's value as a material in agricultural and construction uses has resulted in a plus $400 million per year industry.

During the initial phases of investigation for this study, it became apparent that the most likely markets for byproduct gypsum are in the eastern United States. Most midwestern wallboard markets can be supplied with native gypsum from nearby mines; however, a large percentage of the eastern markets use imported gypsum from Nova Scotia. Therefore, the study was directed toward this market displacement opportunity.

In this feasibility study, six types of processes were considered for byproduct gypsum production. Of the six types, those which produce gypsum by oxidation of calcium sulfite sludge from lime and limestone scrubbing or by neutralizing a weak sulfuric acid scrubbing solution with lime or limestone appear to be the best suited. In Japan, some of these processes are already being utilized to supply gypsum requirements. One of these, the Japanese Chiyoda "Thoroughbred 101" process, is now undergoing prototype plant tests at a Gulf Power Company plant in Florida, and the gypsum produced will be made into wallboard. Definitive test results are expected by the latter part of 1974.

The lack of firm cost data makes it impossible to directly compare the economics of gypsum-producing processes with other SO_2 removal processes such as the lime or limestone throwaway schemes.

However, a gypsum process has two major advantages over a lime or limestone throwaway process.

1. Disposal costs for the calcium solids produced in the throwaway processes are eliminated.
2. Sales revenue most likely can be obtained for the byproduct gypsum.

In addition, in the eastern U.S. where the largest markets are, byproduct gypsum could be shipped to many wallboard plant locations cheaper than imported material. Domestic gypsum is not competitive in this area because of its higher cost ($3.93/ton f.o.b. vs. $2.38/ton f.o.b. in 1972) and the extremely high rail transportation costs from the Midwest mines to the East Coast ($22-$23/ton vs. about $4/ton for water transport of imported material).

Producing byproduct gypsum instead of disposing of calcium solids from the lime throwaway process results in a disposal cost savings of approximately $4.50-$7.00/ton of gypsum. It is probable that the byproduct gypsum can be sold for at least $2.00/ton, $0.38/ton cheaper than imported and $1.93/ton cheaper than domestic gypsum. Byproduct gypsum can also be shipped from steam plants on the inland waterways and along the East Coast to wallboard plants in the same areas from $0.65 to $7.45/ton cheaper than imported gypsum.

The potential economic advantage that byproduct gypsum processes might have in comparison to throwaway systems would, therefore, be the sum of the disposal cost savings, sales revenue, and any transportation credits less any differential in process cost. Depending on the power plant location and processing costs, this advantage over a throwaway process could range from nothing to over $16/ton of gypsum disposed. For a 500-MW power unit, this could be as much as a $3.8 million per year reduction (45%) in the cost of operating a lime scrubbing - solids throwaway system.

This preliminary investigation indicates that production of wallboard - quality byproduct gypsum from SO_2 removal systems may be an economically attractive route to waste solids disposal. It is recommended that a more detailed market study of calcium-sulfur sludge for wallboard be performed. To derive more accurate cost data for comparison with throwaway alternatives, a thorough economic evaluation of the more promising processes such as Chiyoda and carbon absorption plus the oxidation step for conversion of calcium sulfite to sulfate should be made.

PHASE 2 OF THE TVA-EPA STUDY OF THE MARKETABILITY OF ABATEMENT PRODUCTS

Phase 2 is titled, "The Potential Abatement Production Marketing of Elemental Sulfur and/or Sulfuric Acid by the Electrical Industry in the Eastern United States." The study started June 24, 1974, and will run through June 23, 1975. The basic objective is to determine for specific power plant installations using flue gas desulfurization system the potential net sales revenue for byproduct elemental sulfur and sulfuric acid which can be realized from marketing strategies covering the existing acid market, the existing elemental sulfur market, and the growth markets for such commodities.

The study is designed to determine the quantities of byproduct sulfuric acid and/or elemental sulfur which could be produced by air pollution abatement at installations for power plants located in the states bordering the Mississippi River, its navigational tributaries, the Great Lakes, and the East Coast. The study should have general application for the geographic area located east of the Rocky Mountains in the United States.

The depth of data gathering will be increased so that important acid costing characteristics such as age, efficiency, necessity for added pollution control equipment, sulfur receiving, and storage facilities will be refined. Acid transportation methods for each power plant and acid plant will be investigated and accurate freight costs will be determined.

Logistical model requires the generation of hundreds of thousands of freight rates for rail, truck, and barge transportation from (1) existing sulfur sources through terminals to acid plants and (2) from steam plants using flue gas desulfurization systems to acid plants. The strategy is (1) to have TVA Navigation Economics personnel generate a large sample of rates by hand as a check reference (2) a computer system will then be developed to generate those rates as a check and (3) to generate the remaining majority within an acceptable margin of error. The system will be designed such that rate generation for future studies, such as potential relocation of the fertilizer industry adjacent to steam plant areas can readily be made. The study will determine the incremental production tonnages of sulfuric acid or elemental sulfur which can be produced with expected variation during the year in order to meet requirements such as AQCR regulations for specific plant abatement production options. Abatement calculations will be based on the tonnages and sulfur content of coal and/or oil which the electrical industry would plan to use through 1980 at the coal and oil-fired power plants where sulfuric acid or elemental sulfur abatement production is considered. A generalized approach will be used to meet current local emission standards plus applicable case variations based on screening criteria such as age of plant, amount of fuel burned, sulfur content of fuel, plant factor, and site limitations.

One of the more important concepts which will be encompassed in this analysis will be that of consumer surplus. In looking back at the demand curve in Figure 5, the consumer surplus would be measured by integrating the entire area under the demand curve which lies above the net sales revenue prices for TVA abatement acid. Each of the acid producers which purchased TVA acid with the exception of the "swing plant" identified in Table 6 would have paid a higher price for the abatement acid. The model encourages the higher cost inefficient producer to close down his acid plant and buy abatement acid. The relatively more efficient producer continues to produce acid from externally purchased sulfur. Thus, the model promotes and enhances efficient production in the sulfuric acid market.

It is the opinion of the author that there is no one abatement product which will have broad application to all power plant installations in the country. Each utility may enjoy a unique location advantage for marketing a specific abatement product. Perhaps the utilities located in the high calcareous soil areas of the Great Plains should be looking at ammonium sulfate as an abatement product. Most of the soils in this area show moderate to extreme sulfur deficiency. Recycling the abatement sulfur products into the fertilizer industry through an established market (back to the land) offers the greatest imminent social benefit to the American consumer. Agriculture is by far the most competitive sector of the American economy.

United States Environmental Protection Agency
Flue Gas Desulfurization Symposium
Atlanta, Georgia November 4 - 7, 1974

THE PRODUCTION AND MARKETING OF SULFURIC ACID FROM THE MAGNESIUM OXIDE FLUE GAS DESULFURIZATION PROCESS

BY

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ESSEX CHEMICAL CORPORATION

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TABLE OF CONTENTS

Page

Introduction 1009

Sulfuric Acid Operations with Feed from an MgO Regeneration Process

1. Calciner Off-Gas 1011
2. Gas Pre-Treatment 1012
3. Acid Plant Changes - Mechanical 1014
4. Acid Plant Changes - Operational and End Product 1016
5. Costs 1020

Economics of a Sulfuric Acid Plant Related to an MgO F.G.D. System 1020

Example Economics 1021

Summary and Conclusion 1025

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Introduction:

For several years within the chemical industry, many processes have been under development designed to remove pollutant materials from waste gas streams. One example is the Chemico-Basic Magnesium Oxide Flue Gas Desulfurization Process (MgO F. G. D.), particularly as it has been applied to fossil fuel burning electric power plants. This process involves, not only the removal of sulfur oxide pollutants, but also the regeneration of the pollution removing agent, together with the production of a saleable by-product; commercial grade sulfuric acid.

The process is capable of removing 90% of the sulfur dioxide present in the flue-gases of boilers fueled with high-sulfur oil or coal. As has been previously described, it consists of scrubbing the flue-gases on their way to the stack with a slurry of magnesium oxide which reacts with the sulfur dioxide to yield magnesium sulfite. The magnesium sulfite slurry leaving the scrubbers is then partially de-watered by centrifuging; the mother liquor being recycled to the scrubbers while the solids are dried in a direct fired rotary drier to yield dry, crystalline magnesium sulfite. This is stored in silos pending shipment to a regeneration plant located in the immediate vicinity of an existing or new sulfuric acid plant.

The regeneration plant consists essentially of a direct fired calciner in which the magnesium sulfite is decomposed into magnesium oxide and sulfur dioxide gas. The magnesium oxide is returned to storage silos at the boiler plant for reuse, while the sulfur dioxide rich gas from the calciner is piped to the sulfuric acid plant for use as its feed-stock in place of elemental sulfur.(1)

Sulfuric acid has been manufactured at Rumford, Rhode Island since 1929. Essex Chemical Corporation has been manufacturing commercial grade sulfuric acid at this facility since 1966 and has been doing so from magnesium oxide regeneration offgas for the past two years. Until July 1, 1974, the regeneration plant was operated using magnesium sulfite from an MgO F.G.D. demonstration unit located at Boston Edison Company's 150 MW oil fired Mystic Unit No. 6. Following successful completion of this demonstration project, the plant has been operating on magnesium sulfite from a similar MgO scrubbing system on 100 MW of Potomac Electric Company's coal fired Dickerson Unit No. 3.

It will be the purpose of this paper to discuss the differences in sulfuric acid manufacture when fed from an MgO F.G.D. process regeneration facility and when fed by an ordinary sulfur furnace, based on the Essex experience. The discussion will begin with the gas that leaves the regeneration facility and continues through to the point in the sulfuric acid plant where there is virtually no difference between a product stream having come from an MgO regeneration facility or from a sulfur furnace. This will include general descriptions of the processes involved, but since the technology of the individual sub-processes is already well developed and in use in the chemicals industry, extensive detail will be omitted.

Later, some of the economic factors governing the use of MgO process F. G. D. will be discussed.

Sulfuric Acid Operations With Feed from an MgO Regeneration Process

1. Calciner Off-Gas

After dust removal, the calciner off-gas is a gas stream at approximately 100° F, saturated with water and containing 8 to 10% SO_2, 4 to 5% O_2 and the rest predominantly CO_2 and N_2; gases that are inert as far as the acid plant is concerned. Table 1 compares typical calciner off-gas and typical burner gas from a conventional sulfur burner.

Table 1

Comparative Composition of Feed Gas to Sulfuric Acid Unit
Overall Composition, Mole %

Type of Gas	N_2	CO_2	O_2	H_2O	SO_2	Total
Regeneration Facility offgas	73	6	5	7	9	100
Sulfur Burner offgas	79	-	12	-	9	100

The proportions of offgas components can be controlled well within the parameters previously indicated.at the regeneration facility.

Cooling, scrubbing to remove particulates and SO_3, and condensing water out of the hot calciner exit gas is accomplished by a "weak acid" scrubber and packed column after the calciner and before the acid plant. At Rumford the liquid effluent from this step is disposed of outside the plant. However, in a full scale plant with MgO sulfur oxides-in-tail-gas control, this stream could be recycled.

2. Gas Pre-Treatment

In the calciner, a low oxygen level is desirable in that it prevents the oxidation of SO_2 to SO_3 (which would be lost in the gas cleaning step just mentioned) and also prevents the oxidation of $MgSO_3$ to $MgSO_4$. Likewise it is important not to allow the existence of conditions on the reducing side which would aid in the formation of elemental sulfur or of soot, unburned fuel. However, in the acid plant's "conversion" or catalytic oxidation step, it is desirable to have a ratio of O_2 to SO_2 in excess of 1.0 - at least 1.2 to 1. It is thus necessary to provide additional oxygen as air, to the gas stream before the conversion step.

Air is used to strip SO_2 from liquid streams at two points in the process; first at the weak-acid scrubber, and then at the dry tower stripper. Additional air is fed into the gas stream at the dry tower inlet, with quantity regulated manually by monitoring SO_2 and O_2 concentrations. At Rumford, this was readily accomplished using conventional wet chemical methods: The Reich and Orsat analysis. Obviously, electronic instrumentation is applicable here.

Drying the cool gas is the next step, and conventional sulfuric acid driers are used. At Rumford, the gas passes through a 93% H_2SO_4 drying tower that was previously used only for drying air to the sulfur furnace. The dried gas can now serve as gas feed to the sulfur burner if it is desired to burn elemental sulfur as a supplement to the SO_2 from the calciner offgas. This was a standard practice for most of our operations at the Rumford plant.

Since the catalyst's ignition temperature is approximately 800° F, the gas must now be heated to this temperature. Several sources of heat are available and, depending on the acid plant heat balance and whether or not sulfur burning is also a source of SO_2, one or more of these sources may be used. If the regeneration facility is sufficiently close to the acid plant, it might be a source of heat. Since calciner offgas must necessarily be cooled to reduce its water content, it would be an advantage to reduce the heat load on the weak-acid scrubber by transferring the heat to the catalyst feed gas. Other possible heat sources include heat exchangers after the converters and, the heat generated if supplemental sulfur is being burned. By using one or more of these sources and applying proper heat conservation techniques, adequate heat can be obtained.

At Rumford, dried gas from the blower enters the sulfur furnace, where additional sulfur may be burned. The gas then picks up additional heat in the secondary converter's heat exchanger and in the primary converter's heat exchanger, before passing to the top of the first catalyst bed. Temperature control is achieved by bypassing gas around the burner, existing boiler, and the heat exchanger, in a manner readily understood by operators of existing sulfuric acid plants.

After SO_2 - O_2 ratio adjustment, drying and heating, the gas from the regeneration facility is essentially the same as that from a sulfur burner. The only significant difference is a higher CO_2 content in gas from the regeneration facility, and possibly a slightly lower oxygen level.

A pictorial comparison of example methods for treating sulfur burner offgas vs. regeneration facility offgas in a sulfuric acid plant is shown in figures 1 (Dry Gas Plant) and 2 (Wet Gas Plant) respectively (SO_2 - O_2 ratio control is not shown).

3. Acid Plant Changes - Mechanical

The major acid plant changes required are those needed to achieve SO_2 - O_2 ratio adjustment, drying and heating of the gas from the regeneration facility. SO_2 - O_2 ratio adjustment may be accomplished as simply as installing a "T" and valve on the suction side on the acid plant feed fan. Drying may involve the installation of a new vessel for 93% H_2SO_4 drying of either regeneration offgas or sulfur furnace feed gas, or both, if existing equipment cannot be refitted for this use. For heating, the proximity of the regeneration facility to the acid plant becomes important if the heat available in the regeneration facility is to be used by the acid plant. For heat conservation, insulation integrity

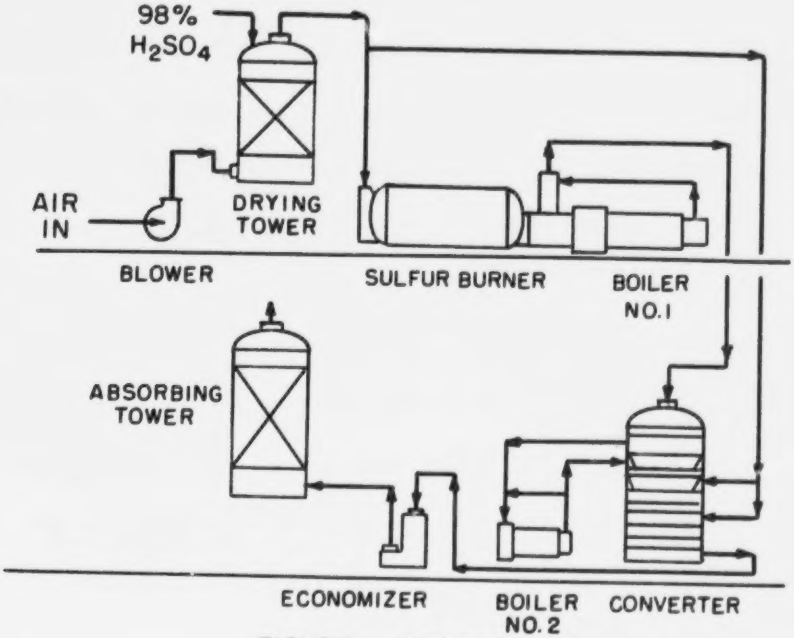
98%
H_2SO_4
AIR
IN
DRYING
TOWER
BLOWER
SULFUR BURNER
BOILER
NO.1
ABSORBING
TOWER
ECONOMIZER
BOILER
NO.2
CONVERTER

FIGURE 1. DRY GAS PLANT

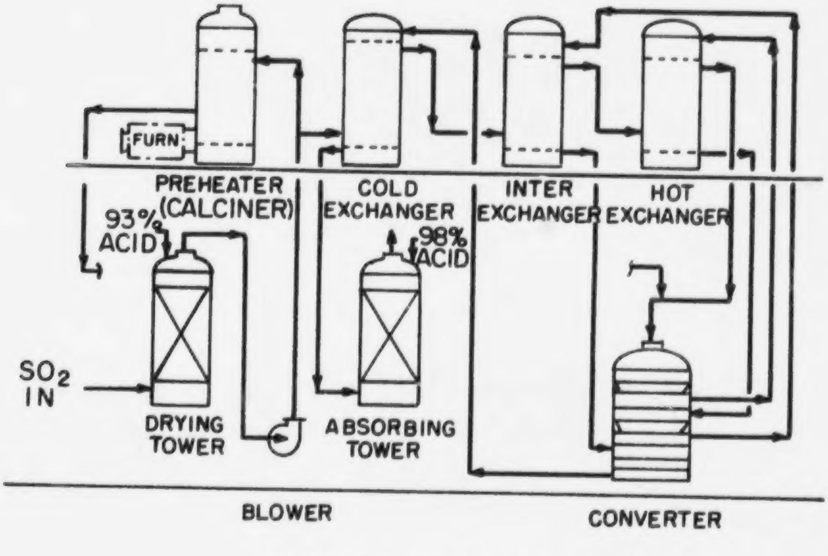
FURN
PREHEATER
(CALCINER)
COLD
EXCHANGER
INTER
EXCHANGER
HOT
EXCHANGER
93%
ACID
98%
ACID
SO_2
IN
DRYING
TOWER
ABSORBING
TOWER
BLOWER
CONVERTER

FIGURE 2. WET GAS PLANT

is a must as is the operation of process flow controls such as dampers and condensate traps. For both drying and utilization of available heat, a considerable amount of repiping was required at Rumford, and will be required in any retrofit installation.

Process control changes are also required. The advent of the additional heat balancing requirements makes process control more complex. Where sulfur burning is used simultaneously with regeneration offgas, blending the streams is also a process control complexing factor. The needed controls are all standard and, as such, there is nothing unproven required. However, there is no question that the control of the efficiency of each subprocess is more critical than if the sulfur burner is the only feed source to the acid plant.

To meet environmental requirements, most acid plants have recently had to exercise greater controls or install abatement equipment to reduce emissions of sulfur oxides to the atmosphere. The control techniques employed are generally designed to either add conversion steps to the process or to absorb or scrub the sulfur oxides out of stack gases. With a regeneration facility in close proximity to the acid plant, it becomes quite economical to install an MgO scrubber as the sulfur oxide emissions control for a new or existing acid plant.

In addition to controlling emissions this increases the sulfur efficiency of the plant. This can make an MgO scrubbing installation for an acid plant being fed by a regeneration facility much more of an economic advantage since it can potentially eliminate the need for capital investment in sulfur dioxide conversion steps.

One other change must be considered and this relates to provisions in the event of an unexpected shutdown of the acid plant. In that event, the regeneration facility normally has considerable surge in the gas stream which cannot be stored. Under these conditions there must be provisions made in the acid plant to take that gas. If an MgO scrubber is installed on the acid plant, the scrubber and appropriate emergency by-pass controls could be designed and installed to control and recover the gas surge from the regeneration facility.

Obviously other currently available technology could be employed to control stack exit SO_2 concentrations: an alkali scrubber, molecular sieve absorbers, or a double catalysis - double absorption flow sheet could be used. At Rumford, SO_2 concentrations from this small obsolete sulfur burning plant were approximately 3, 500 ppm before the MgO regeneration facility was installed. Because of the relatively short life of the project, Chemico installed a simple scrubber on the acid plant stack, using caustic soda as scrubbing liquor to control SO_2 discharge which might be as high as 4, 500 ppm when the calciner was operating. No attempt has been made to maximize the performance of this small scrubber, and a local contractor is used to haul away the spent alkali.

4. Acid Plant Changes - Operational and End Product

All operational changes occur in or before the converters. As indicated before, where a regeneration facility and a sulfur furnace are used simultaneously, the blending of these streams places additional requirements on control of the heat, SO_2 and O_2 content of the gases fed to the converters. This is a new type of operation which required the development of new techniques at Rumford. Also, where the regeneration facility, the sulfur furnace, and/or the converters are used to heat the dried gas from the regeneration facility, new start-up techniques may be required. At Rumford, for both start-up and operation, these requirements amount to adjusting the ratio of air to regeneration facility offgas being fed to the drying tower since this is the atmosphere in which any supplemental sulfur burning is done. From the sulfur furnace through the rest of the acid plant, the start-up techniques at Rumford have not changed and the techniques used to maintain heat balance in the plant after start-up are the same type as those used in a conventional sulfur burning contact sulfuric acid plant.

The water balance in the plant also becomes more critical with the additional water input from regeneration offgas, but again, the techniques used for control are the same type as those used in a conventional sulfur burning plant. Past the converters, the operation is identical to that of a conventional plant.

Since the gas fed to the converters is virtually the same as with a conventional plant it would be expected that the end product would also be the same. This has been the case in Essex' experience when the regeneration facility is operating on feed from either an oil fired or a coal fired power plant.

Sulfuric acid meeting Federal specifications for electrolyte acid (50 ppm Fe maximum) can be routinely produced from MgO regeneration offgas, in any desired concentration up to the limit of the plant's capability, and consistent with water balance. At Rumford, we historically produced acid with Fe content in the 12 to 14 ppm range during the winter months. In summer, with higher metal temperatures exposed to our product, it was rare for iron content to be much above 25 ppm.

In the opinion of our plant management, acid quality has not varied significantly with the advent of the regeneration facility; iron content runs approximately 20 ppm. There has never been any finding of magnesium compounds in the product acid.

Rumford sulfuric is all sold in merchant market, and none is used captively. We sell product to manufacturers of detergents, dye-stuffs, pharmaceuticals, and tanning chemicals; to steel companies for pickling; to utilities for boiler water treatment; to water and paper companies for pH control; to manufacturers of aluminum sulfate; to galvanizers; to a wider range of textile applications; to manufacturers of lead-acid storage batteries, etc., etc.

By and large, Essex sales in the New England market are at the full published price, which is at this writing $45.95 per ton, basis

100% H_2SO_4. Producing sulfuric acid from MgO regeneration offgas has imposed no restrictions on Essex marketing of that sulfuric acid.

5. Costs

Capital costs for modification of a new or existing sulfuric acid plant for use of MgO regeneration offgas as feed to the plant typically run less than 15% of the battery limits capital cost of the plant. Operating cost additions are minimal and consist mostly of power to transport the additional gas and liquid streams. No additional manpower is necessary and no significantly different maintenance is required.

Economics of a Sulfuric Acid Plant Related to an MgO F.G.D. System

It has been demonstrated that the construction and operation of MgO F.G.D. scrubbers and regeneration facilities represents an economically attractive alternative to burning low sulfur fuels in many electric power utility applications. What has not been previously discussed is the economics of the sulfuric acid plant portion of the system and the relationship this has to the overall economics of the system. This section will undertake that discussion and present an example of the acid plant's operating economics.

The approach used here will be from that of a sulfuric acid manufacturing company constructing and operating the plant, selling its output in the conventional manner and deriving the profits that would provide the motivation for such a company to enter into this business. It is recognized that through capital or other means, the utility or other parties might participate in the acid plant economics. However, it is not expected that utilities will desire to operate a chemical process facility. In the example to follow it will be assumed that the applicable acid plant economics are those of a chemicals manufacturing firm.

Example Economics

To determine the acid plant size required in this example, it will be assumed that the plant is to match an F.G.D. system on a 1,000 MW electric power plant operating at 75% load factor and burning 3% sulfur oil. From Appendix I, 90% sulfur oxides recovery will result in the production of 126,710 short tons of sulfuric acid per year. This would indicate that the design basis should be for a 400 ton per day acid plant. The current estimated capital cost for such a facility; including battery limits and off-site facilities, design, engineering, purchase and erection (escalated through 1977) and not including land, working capital, and financing costs, is $6,750,000. For this example a 15% return on investment after taxes will be considered sufficient justification for the construction of the plant.

The operating costs will be based on current costs escalated through 1977 at 7% per year. Conventional financing will be assumed for all of the capital cost at 12% interest per year.

While the price per ton of sulfuric acid at this writing has been quoted as $45.95, a more conservative position will be used here. For this example, it will be assumed that the market exhibits some saturation above 100,000 short tons per year in this way: The first 100,000 tons will return $30.00 per ton net back at the plant and all above 100,000 tons returns $5.00 per ton. Under these conditions, for the 126,710 tons under discussion, the gross revenue would be $3,133,550.

The object of this example will be to determine the dollar value of the sulfur oxides required to provide the economics indicated above.

Actual Capital Required

Capital (as stated above)	$ 6,750,000
Land (5 acres at $50,000 per acre)	250,000
Working Capital	1,000,000
Interest During Construction (2 years at 12%)	1,680,000
Total	$ 9,680,000

ROI Required

9,680,000 X 15% = $1,452,000 Per Year After Taxes

Interest Charges

$6,750,000 financed at 12% interest for 30 years would require yearly capital charge payments of $710,190 of which an average of $485,190 would be interest.

Operating Costs

It is assumed that the acid plant would use MgO stack gas scrubbing for SO_2 emissions control.

	Unit	Unit Cost	Amount	Annual Cost
Variable Costs				
Cooling and Process Water	Gal.	\$.655/1,000	69,394 M	\$ 45,453
Electric Power	KWH	\$.034	9,784 M	332,656
MgO	Ton	\$123.00	1,972	242,556
Catalyst	Per Ton of H_2SO_4 Produced	\$.1225	(126,710)	15,522
Cooling Water Treatment	Per Ton of H_2SO_4 Produced	\$.08	(126,710)	10,137
Sub Total				\$ 646,324
Non-Variable Costs				
Direct Labor			13 People	230,778
Office & Supervision			5 People	100,375
Maintenance Labor & Material			5% of Initial Capital	337,500
Laboratory and Supplies				21,875
Equipment Rental				4,000
Insurance and Taxes (2% of Capital)				135,000
Depreciation (10 Year)				968,000
GS& A (7% of Sales)				219,344
Sub Total				\$ 2,016,877
Total				\$ 2,663,201

Total Cost vs. Return

Under these conditions, the total annual cost to operate the acid plant would be:

Operating Costs	$ 2,663,201
Interest Charges	485,190
Income Taxes	1,340,308
Return on Investment	1,452,000
Total	$ 5,940,699

To balance this, returns to the acid plant operation would be required as follows:

Sulfuric Acid Sales	$ 3,133,550
Support from F.G.D. User (The Utility)	2,807,149
Total	$ 5,940,699

From data in Appendix I, it can be calculated that support from the F.G.D. user is equivalent to $.304 per barrel of fuel oil used or 0.44 mils per KWH of power generated by the F.G.D. user.

It must be emphasized that this is one very specific example and that wide variations from this example would be common. Varying acid market price, transportation costs, fuel costs, capital costs, and method of financing could all significantly affect the sulfuric acid plant economics. Also, capital participation on the part of the F.G.D. user could considerably reduce the expense of support requirements on the F.G.D. user by reducing the return on investment requirements of the sulfuric acid manufacturer. Depending on the degree of participation (for example, if funds were provided for the sulfuric acid plant from the same source that they were provided for the rest of the F.G.D. system, making the investment one complete package), in the specific example herein stated the support requirements could be reduced by more than 80% or down to less than $.06 per barrel or 0.09 mils per KWH.

Likewise if the sulfuric acid plant being used in the F.G.D. system is an existing plant, the only requirement for capital is for retrofit which, as was mentioned before herein, is a considerably smaller investment. Under these circumstances also, the return on investment requirements (and thus F.G.D. user support) would be considerably less and, with F.G.D. user capital participation, still less than what was shown in the example given.

Summary and Conclusion

The technical feasibility of the use of SO_2 gas recovered from MgO regeneration as the feed to a sulfuric acid plant has been demonstrated at Essex' 50 ton per day sulfuric acid plant at Rumford. The techniques and changes required to accomplish this have generally been described here and, for two years electrolytic grade sulfuric acid has been produced and sold from gas coming from an MgO regeneration facility. Technical feasibility is established.

As also described herein, the economics of the MgO process will vary with location. However, the most favorable applications are those in urban locations, where offgas can replace sulfur in captive sulfuric acid plants, where significant cost advantages accrue from power plant use of high sulfur fuel, where freight rates from an MgO source are not prohibitive, where the installation is new or retrofit is not complex, and where local regulatory agency rulings permit equitable distribution of F.G.D. costs to the rates and promote reasonable capital financing. Where enough of these conditions exist, the MgO F.G.D. system can be a low cost environmental advantage to the public, the most appropriate and economic F.G.D. system for the utility and a viable service business for the sulfuric acid manufacturer. Essex Chemical Corporation plans to participate fully with Chemical Construction Corporation and Basic Chemicals Inc., in the installation and operation of future electric power plant MgO Process Flue Gas Desulfurization Systems.

Appendix I

Sulfuric Acid Plant Requirements

Based on Utility Capacity

Data

Station Rated Capacity	1,000 MW
Station Heat Rate	9,000 BTU/KWH
Fuel	3% Sulfur Oil
Load Factor	75%
Fuel Heat Content	18,500 BTU/lb.

338.1 lb. Oil = 1 Bbl. Oil

90% of sulfur oxides removed by F.G.D. system.

96% of recovered sulfur oxides converted to H_2SO_4.

Total BTUs Required Per Year

1,000,000 KW X 8,760 Hr. X 9,000 BTU/KWH X 75% =

59.13 X 10^{12} BTU/Yr

Total Oil Required Per Year

$$\frac{59.13 \times 10^{12} \text{ BTU/Yr}}{18{,}500 \text{ BTU/lb} \times \frac{338.1 \text{ lb}}{\text{Bbl}}} = 9{,}453{,}464 \text{ Bbl/Yr}$$

Total Sulfur Recovered Per Year

$$9{,}453{,}464 \text{ Bbl/Yr} \times 338.1 \text{ lb/Bbl} \times \frac{1 \text{ long ton}}{2{,}240 \text{ lbs}} \times .03 \times .9 =$$

38,526 Long Tons/Yr

Total Sulfuric Acid Generated Per Year

$$38{,}526 \ \frac{\text{Long Tons}}{\text{Yr}} \times \frac{3.426 \text{ Short Tons } H_2SO_4}{\text{Long Ton Sulfur}} \times .96 =$$

126,710 Short Tons/Yr

Appendix II

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SECOND GENERATION PROCESSES FOR FLUE GAS DESULFURIZATION

INTRODUCTION AND OVERVIEW

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INTRODUCTION AND OVERVIEW

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The earlier papers in this symposium dealt with processes that have been operated on a full scale. There is also a large group that are not as far along and therefore can be said to be in the "second generation" category. Examples of these can be found in each of the three major process groups: (1) lime-limestone scrubbing, (2) two-stage (or indirect) lime-limestone (clear liquor scrubbing with lime-limestone regeneration, often called "double alkali"), and (3) recovery of the sulfur as a useful product. The present paper introduces the "second generation" category and attempts to analyze the merits and drawbacks of each of the processes involved.

What is a second generation process? This is a good question, because process status ranges all the way from systems that are fairly well developed to nebulous departures that have not yet reached the laboratory bench. There is no sharp dividing line at any stage that allows a good classification between the first and second generation, or that qualifies a process for the second generation category rather than perhaps "third generation." In this paper a process must have been tested at least on a pilot-plant scale to qualify. At the other end of the spectrum, methods that have been tested on a full scale are generally excluded but a few of those developed recently in Japan are included because they are new to the U. S.

Lime-Limestone Scrubbing

Since absorption of SO_2 by a lime or limestone slurry is the oldest and most used technology, most of the process variations can be regarded as first generation. The few that seem to fit into the second generation category are listed in Table 1.

Fuji Kasei (Japan)

The main feature of the Fuji Kasei process is a special scrubber (called "Moretana"), which contains four perforated plates each with the hole diameters and plate thickness tailored to the specific scrubbing situation. The system has been installed on three industrial boilers. A special oxidizer is used to convert the calcium sulfite to gypsum.

Fuji Kasei claims an exceptionally high mass transfer rate for the Moretana scrubber. The system has made little headway, however, against the lime-limestone system of Mitsubishi Heavy Industries. Although 13 Fuji Kasei installations are said to be planned, they are all on small industrial boilers or other small units whereas MHI has many systems installed or underway in plants of the major Japanese utilities.

Joy Manufacturing

A wet precipitator placed on top of a spray scrubber removes mist and fine particulate. A pilot plant is operating at Pennsylvania Power and Light's Sunbury station.

Another feature of the process is a very high L/G that gives high scrubbing efficiency and utilization even though limestone is the absorbent. Mist elimination and particulate removal are also good; the pilot plant has a clear stack.

The high efficiency of wet precipitators in removing fine particulate ($< 2\ \mu$) may give the Joy system added significance in the future, especially if the absorber can remove the bulk of the dust without fouling. No precipitator would then be necessary ahead of the scrubber and the wet precipitator would give better overall efficiency than the usual combination of dry precipitation and wet scrubbing.

Kellogg

Magnesium compounds are added to the lime-limestone slurry in fairly large amounts to improve absorption efficiency and promote oxidation to sulfate. Excellent results were obtained in pilot-plant tests. Since much of the absorbed SO_2 is present as dissolved magnesium sulfite and bisulfite, oxidation can be carried out by air sparging without the expensive pH control necessary in Japanese processes for oxidizing calcium sulfite.

If the process is shown to be effective on a larger scale, it may be widely adopted. The gypsum produced should be a superior throwaway material.

Mitsui Miike

This is another process for getting sulfite oxidation without using sulfuric acid to lower the pH as is done in most Japanese lime-limestone processes. The bleed stream from the scrubber, on its way to the oxidizer, is contacted with about 25% of the unscrubbed stack gas. The resulting partial SO_2 absorption reduces the pH enough to get the calcium sulfite in solution and available for oxidation. The gas stream then passes to the main scrubber to complete the SO_2 absorption.

An unidentified catalyst is used to increase both oxidation rate and absorption efficiency. Pilot-plant data have indicated good efficiency with limestone even in venturi absorbers.

A prototype is just starting up in Japan and construction of units for three boilers is underway. Further adoption depends on the balance between the relatively high investment and the reduced operating cost. (See further discussions in a paper by J. Ando in this symposium.)

National Lime Association

A rotary drum fitted with hanging chains inside serves as the scrubber. Several advantages are claimed, including (1) no possibility of scaling, (2) low pumping head, (3) low pressure drop, (4) no lime slaking or gas prehumidification needed, (5) no nozzle wear, and (6) no demister plugging.

Four pilot plants have been operated. The data do not appear sufficient for fully evaluating the process. It is reported that an industrial boiler will be fitted with the system, in which case a good evaluation probably can be obtained. The potential advantages make the process very attractive if absorption efficiency is adequate and if dust evolution is not a problem.

TVA

The use of a small amount of benzoic acid improved limestone scrubbing efficiency in pilot-plant operation. A cost estimate made by TVA, however, indicates that the overall economics may not be favorable (see paper by G. G. McGlamery in this symposium.)

Evaluation

The second generation approaches in lime-limestone scrubbing are not likely to have as much impact as in the double alkali and recovery areas. The first generation systems are becoming reasonably well developed--especially those at Paddy's Run and Mohave which seem to be operating fairly reliably. Nevertheless, the promise of lower cost and superior product may give the new processes an important role.

Lime-Limestone: Two-Stage Operation (Double Alkali Type)

The scaling and plugging problems encountered in lime-limestone scrubbing have led many investigators to look for a better throwaway method. Most of the effort has been on the approach of using a clear solution in the scrubber and reacting the scrubber effluent solution with lime or limestone to precipitate calcium sulfite and sulfate, the same products as in straight lime-limestone scrubbing. The absorbent is usually a solution of ammonia or a sodium salt (whence the term "double alkali") but several other materials have also been used.

The process list in Table 2 includes the first generation processes for perspective. About half of the methods are in the second generation category, indicating the high degree of development activity in the field.

Chiyoda (Combined NO_x-SO_2 Process)

The standard Chiyoda process (catalyzed weak acid scrubbing followed by reaction with limestone) has been combined with NO_x removal by adding ozone to the entering gas stream. One of the products is nitric acid, which is collected in the scrubber. The method is considered to be especially suitable for use in conjunction with the main Chiyoda process because otherwise the nitric acid would cause undesirable sulfite oxidation, whereas Chiyoda is a full-oxidation process (see paper in this symposium).

The growing emphasis on NO_x emission reduction in Japan may bring processes such as the Chiyoda NO_x-SO_2 combination into use. The method seems to have some advantage over those that remove NO_x and SO_2 in separate, unrelated operations. Further tests on a larger scale are necessary for adequate evaluation.

Fuji Kasei (Japan)

This is also an SO_2-NO_x combination method, with sodium hydroxide used as the SO_2 absorbent and lime as the regenerant. Chlorine dioxide is added just before the scrubber to oxidize NO. It is claimed that the oxidation is selective and that little ClO_2 is lost in oxidizing SO_2.

Since some phases of the process have not been worked out, evaluation is difficult. Five installations on industrial boilers are being considered.

Kurabo (Japan)

In the absorber loop, a solution of ammonium sulfate is circulated through the scrubber and then through an air oxidizer. A bleed stream from the oxidizer is treated with lime to precipitate calcium sulfate.

Kurabo has tested the process at the company's pilot-plant installation near Osaka (Japan) with good results. The ammonium sulfate provides enough basicity to absorb SO_2 efficiently at a medium L/G (in the 50-80 gal/mcf range, depending on process requirements). Thus the process is in between Chiyoda and double alkali processes such as Kureha-Kawasaki and Showa Denko, in which Na_2SO_3 is the absorbent, lime or limestone is the regenerant, and the calcium sulfite is oxidized in a system requiring addition of sulfuric acid. Kurabo has a lower L/G than Chiyoda but retains the Chiyoda advantage of oxidizing sulfite while it is still soluble rather than after conversion to calcium sulfite.

The method is also superior to ammonia-based double alkali processes (NKK, Kuhlmann) in that the regenerated ammonia is recycled as aqueous ammonia rather than in the gaseous form, thereby avoiding the need for an ammonia recovery scrubbing system. In addition, there is no fume formation in the Kurabo process; although it may be possible to avoid fuming in ammonia scrubbing methods, special care will be required and some additional expense involved.

Kurabo is building full-scale systems, one of which is to start up this year. The system is described more fully in a paper by J. Ando in this sypmosium.

Dowa Mining (Japan)

The SO_2 is absorbed in a solution of $Al_2(SO_4)_3 \cdot Al_2O_3$, giving $Al_2(SO_4)_3 \cdot Al_2(SO_3)_2$ which is then oxidized to $Al_2(SO_4)_4$ and regenerated with limestone.

The process has advantages similar to the Kurabo method--lower L/G than for water or weak acid scrubbing and easier oxidation than for sodium or ammonia-based double alkali processes. As compared to Kurabo, the ability to use limestone rather than lime is a definite advantage.

Dowa Mining has installed the aluminum sulfate process on two of its own sulfuric acid plants. These were started up quite recently; operation so far seems to be satisfactory. (See also discussion in the symposium paper by J. Ando.)

Lurgi

The Lurgi double alkali process is a $NaOH$-$Ca(OH)_2$ system much like the General Motors double alkali process in the U. S. (see paper by N. Kaplan in this symposium), except that a special scrubber type is used. Pilot-plant work has been carried out but apparently no commercial units have been installed.

Monsanto

A water solution of ethanolamine absorbs the SO_2 followed by regeneration with lime. A 1-mw pilot plant has been operated and a 125-mw design prepared. The process is described in detail and the advantages presented in a later paper in this symposium.

Toyo Engineering

The system is of the ammonia-lime type. The main distinctive feature appears to be use of a special crystallizer design in reacting the $Ca(OH)_2$ with the ammonium sulfites and sulfate.

The status of the Toyo process is not clear. No units have been sold and the company does not seem to be developing the process further. No evaluation can be made until further information is available.

Evaluation

The impact of the second generation processes in the two-stage throwaway field is not very clear. While some of them have significant potential advantage over the first generation group, the situation is clouded by the fact that two-stage processes in general may not be able to compete with direct lime-limestone scrubbing. The two-stage type was developed primarily to avoid scaling and plugging in the scrubber, but recent improvements seem to have essentially eliminated this problem in direct scrubbing.

Processes based on sodium or ammonium compounds as absorbents have the advantage, however, that a very high degree of SO_2 absorption can be attained, thus giving the two-stage type an advantage in situations where high removal is required. If the cost can be reduced by second-generation departures, and added advantages such as NO_x removal developed, the position of two-stage throwaway may improve in the future.

Recovery

The sludge disposal problem in the foregoing processes is enough in itself to make recovery of the sulfur in a salable form an attractive course. In addition, sale of the product offsets to some extent (usually very small) the cost of the operation, and a natural resource is conserved that otherwise would be wasted as sludge. The last of these is especially important because it is likely in the future that sulfur recovered from waste gases will be needed to bolster the dwindling supply from other sources.

Processes in the recovery category outnumber the throwaway type by a considerable margin; a hundred or more can be counted if those patented but relatively untested are included. The list in Table 3 includes only the more significant ones. Again, the first generation methods are listed to give perspective.

Development work on recovery processes has followed four major lines of attack.

1. "Gathering" the SO_2 in a concentrating operation to get a stream concentrated enough for economical conversion to sulfur or sulfuric acid. Sulfur is the preferred product because storage is simpler and shipping cost lower.

2. In situ oxidation or reduction of the SO_2 while still in the main gas stream. Because of the dilute concentration, this has been a difficult technology to develop.

3. Collection of the SO_2 as an alkali, sulfite, followed by reduction in a high temperature process, separation of H_2S in an intermediate step, and conversion to a sulfur by the Claus or other standard process.

4. Reduction of alkali sulfite at low temperature while still in solution. Elemental sulfur may be produced directly in the solution, as in the citrate and phosphate methods, or H_2S can be evolved as an intermediate. Such processes generally depend on formation of thiosulfate in the solution since it appears that thiosulfate is easier to reduce to sulfur or hydrogen sulfide than are most other sulfur compounds.

The first-generation recovery processes have several problems that are either not encountered or are less troublesome in throwaway methods.

1. Dust in the gas, even though mainly removed in a preceding precipitator, can accumulate in closed-loop scrubbing and regeneration systems, and interfere with operation. And if a catalyst is used, blocking of the pores can be a problem.

2. Processes are relatively complicated and expensive because of the regeneration requirement.

3. Energy requirement in the regeneration step can be quite high.

4. If the reducing agent is natural gas, it may well be not only expensive but also unavailable. (EPA has a program underway on developing ways to use less expensive reducing agents.)

5. If the reducing agent is hydrogen sulfide, it will have to be made in most cases by reducing two-thirds of the product sulfur--which is expensive and involves handling large quantities of a relatively hazardous chemical.

6. Unless the process can reduce sulfate as well as sulfite, the high solubility of the sulfate will cause a water pollution problem.

7. The product must be moved out to consumers on a fairly steady basis since it cannot be discarded unless special provisions are made (neutralization of acid or landfill of sulfur). This is much more of a problem with acid than with sulfur because the latter can be stored at relatively low cost.

On the other hand, recovery has an advantage over the lime-limestone processes in that there is the opportunity for operating in the dry state and thus avoiding the need for reheating the gas.

The ability to avoid one or more of the problems unique to recovery is a major advantage for any recovery process. The main effort in second-generation process development has been to avoid as many of them as possible and thus to improve over the first generation type.

Gathering Processes

Methods that concentrate the SO_2 as a first step include both alkali solution scrubbing and absorption in solids at elevated temperature.

Alkali Scrubbing: The Stone and Webster-Ionics process is based on scrubbing with Na_2SO_3 solution. The Na_2SO_3-$NaHSO_3$ from the scrubber is treated with a Na_2SO_4-H_2SO_4 solution equivalent to sodium bisulfate to evolve a rich stream of SO_2 and the coproduct Na_2SO_4 electrolyzed to regenerate the bisulfate. Power consumption is high but the cost can be minimized by using off-peak power. Excess sodium sulfate caused by oxidation must either be discarded or electrolyzed to give weak sulfuric acid, which is probably usable if H_2SO_4 is the main product. Further evaluation of the process is given in another paper in this symposium.

In the ammonia scrubbing process being developed by EPA-TVA, the ammonium sulfites produced in the scrubber are decomposed in a way similar to S and W-Ionics--by treating with ammonium bisulfate. The bisulfate is regenerated thermally rather than by electrolysis. Excess sulfate must be separated but since it is ammonium sulfate it can be used as a fertilizer. This process is also evaluated further in another symposium paper.

The IFP ammonia scrubbing method involves evaporation of the scrubber solution to give a gaseous mixture of SO_2, NH_3, and H_2O, which is then mixed with H_2S and passed through the IFP "wet Claus" reactor. Elemental sulfur is formed directly and the ammonia, which is not affected, is returned to the scrubber. A separate step is provided for reducing excess sulfate.

The IFP method is being tested, both in prototype and full-scale units, in France and Japan. None of the installations has been operating long enough to provide any significant data. Like the EPA-TVA process, there is a fume problem in the scrubbing step. Progress has been made in preventing the fume but further demonstration is needed.

Absorption in Solids: The Esso-B and W method is reported to be of the solid absorbent type. Pilot-plant work has been underway for some time but no data have been reported. The dry operation avoids the corrosion and other problems encountered in wet scrubbing and no reheat is necessary. The equipment is large because of the high operating temperatures, however, and the absorbent is subject to plugging by dust.

The Bergbauforschung carbon process is also of the gathering type. The sorbed SO_2, converted unavoidably to H_2SO_4 in the carbon pores, is evolved as a concentrated stream by heating the loaded carbon to a temperature high enough for reduction of the acid by part of the carbon. The method will be tested in a prototype at Gulf Power's Scholz station.

Although the Bergbau process involves handling large tonnages of moving solids, the system is dry, can be added at the end of the power plant train, and removes dust from the gas without any adverse effects on regeneration.

All the gathering processes require a second operation to convert the SO_2 to a useful product. Making sulfuric acid is the simplest approach but several methods for making sulfur are being explored. The first generation method (but still not demonstrated for power plant operation) is reduction by natural gas. Foster-Wheeler is working on a second-generation process in which the reduction is accomplished by direct reaction with anthracite coal. This will be tested in conjunction with the Bergbauforschung test project.

Oxidation in Situ

The Westvaco carbon method appears to fit best into this category. The sulfuric acid formed in the carbon pores by SO_2 oxidation is converted directly to elemental sulfur by reduction with H_2S, after which the carbon is heated to volatilize the sulfur.

The Westvaco method is dry, is not affected by dust, uses coal (converted to producer gas) as the reductant, and has no sulfate problem. The main question may be the carbon attrition in the fluidized bed adsorber. Further evaluation is given in another paper in this symposium.

High Temperature Reduction

The main example is the Atomics International method in which the SO_2 is absorbed by a molten mixture of alkali carbonates and the resulting sulfites reduced to sulfide by reaction with petroleum coke at high temperature. The sulfides are then dissolved in water and CO_2 added to evolve H_2S which is converted to sulfur by standard procedures. Tests of the method in a 10-mw system at Consolidated Edison's Arthur Kill station have encountered severe corrosion problems.

The basic reduction step in the molten salt process has been used by AI in another system (aqueous carbonate) that operates at lower temperature and therefore can be added at the end of the power plant train. Sodium carbonate solution is sprayed into a spray-dryer type of absorber in which the solution absorbs SO_2 and is evaporated to dryness. The solid sodium sulfite is reduced with coke and H_2S produced as in the molten salt process.

The water evaporation cools the gas somewhat but not as low as a wet scrubber; reheat probably would not be required. Petroleum coke is an economical reducing agent, all the sulfate is reduced by the coke, and sulfur is the product. Thus the process avoids the problems mentioned earlier; on the other hand, a particulate collection system must be installed after the scrubber to recover the sodium sulfite.

The spray drying and reduction steps have been tested separately in pilot plants and the H_2S generation is a common process in the paper industry. An integrated test program is needed.

In Japan, Tsukishima Kikai (TSK) has adapted the Billerud process to SO_2 recovery from stack gases. The Billerud is a method used in the paper industry to recover sulfur compounds from waste lignin-bearing liquors. The liquor is sprayed into a furnace fired with heavy oil under reducing conditions. The organic compounds in the liquor reduce sodium sulfite and sulfate to sodium carbonate (solid) and H_2S. The sodium carbonate is separated, along with carbon formed because the furnace is operated at a temperature low enough to prevent melting of the sodium carbonate, and the H_2S converted to compounds for recycling.

In adapting the process to stack gas cleaning, TSK operates much like the Billerud method. Stack gas is scrubbed with recycled sodium carbonate solution and the resulting sulfite-sulfate solution sprayed into the top of a standard Texaco or Shell oil gasification unit. The solids-laden gas passes through a waste heat boiler, a cyclone-scrubber combination to separate the solids, and a Stretford unit to convert H_2S to elemental sulfur.

The method uses a low-cost reducing agent, has a relatively low regeneration energy requirement, and produces sulfur. The main problems are the dilute concentration of H_2S in the gas and difficutly in separating carbon. Pilot-plant tests are underway.

Reduction in Solution

The citrate process has been developed mainly by the U. S. Bureau of Mines. Pfizer also is doing development work on the method. The SO_2 is absorbed in sodium citrate solution and the scrubber effluent treated with H_2S to give elemental sulfur directly. Although the chemistry is not entirely clear, thiosulfate is formed during regeneration and probably is the material actually reduced to sulfur. The citrate buffers the system and keeps it in a desirable pH range.

In addition to work in the Salt Lake City laboratories, the Bureau is operating a pilot plant (about 0.5-mw) at the Bunker Hill smelter in Kellogg, Idaho. A unit for producing H_2S from product sulfur is included. Pfizer has a pilot plant at Terre Haute, Indiana, quite similar to the Bunker Hill pilot except that a different flotation system is used to separate the finely divided sulfur from the citrate solution and no H_2S production unit is included. Both pilot plants seem to be giving good results; the Bunker Hill operation is described in one of the following papers in this symposium.

Stauffer has a variation of this type of process, with phosphate used as the buffering agent. A small pilot plant (about 300 cfm) is being operated at Northeast Utilities' Norwalk Harbor station. This operation is also much like that at Bunker Hill excpet for a different flotation system. Results are reported to be good.

All three systems produce sulfur and have a relatively low energy requirement. The drawbacks are very dilute scrubber solution (with consequent large regeneration system size), use of H_2S as the regenerant, natural gas requirement to make the H_2S, and a purge stream of sodium sulfate (although not as much as in the Wellman-Lord process).

The Consolidation Coal method has been disclosed only in patents, which indicate that the scrubbing solution contains potassium compounds such as K_2CO_3, KOOCH, KSH, and K_2S; that potassium thiosulfate ($K_2S_2O_3$) is a major product; and that the $K_2S_2O_3$ is reduced to H_2S by use of CO. The chemistry is complex and many side reactions occur. The scrubbing step has been tested on a 10-mw scale and regeneration in a small pilot plant (less than 0.5-mw).

UOP's Sulfoxel process has also been described only in patents. These indicate scrubbing with an alkali such as Na_2CO_3, treating the resulting sulfites with H_2S to form thiosulfate, reducing the thiosulfate to sulfide by use of CO, and carbonation of the sulfide to evolve H_2S and regenerate Na_2CO_3. Part of the H_2S is recycled and part converted to sulfur as the product. A 22-mw test system installed at Commonwealth Edison's State Line station was shut down recently and tests begun on a smaller scale.

Evaluation

From this it is clear that the second-generation recovery methods avoid some of the problems that are drawbacks to the first generation. Some of the processes are more successful than others in this respect.

In regard to plant cost, it is difficult to make an evaluation because none have been developed far enough for definitve cost estimates. The carbon processes have the drawback of very large absorbers, and the regeneration solutions in the citrate and phosphate methods are so dilute that large equipment will be required. The ammonia systems are superior in this respect but extra capital may be required for fume control. The TSK is quite straightforward but, again, the H_2S stream is dilute. The electrolytic cells in S and W-Ionics and the spray drier in AI's aqueous carbonate are expensive pieces of equipment. Both Consolidation Coal and UOP appear to be relatively complex processes.

Energy requirement for regeneration appears to be relatively low for AI's aqueous carbonate, citrate-phosphate, TSK, and Westvaco. Moreover, AI, Westvaco, Bergbau, and Esso-B and W save energy by not requiring reheat.

In regard to type of reducing agent, the ability to use petroleum coke by AI and heavy oil by TSK is major advantage. Foster-Wheeler, which has licensed Bergbau, also is developing an SO_2 reduction method based on coal. Methods such as BM, Pfizer, Stauffer, and Westvaco, that use H_2S as a reducing agent, are under a burden because of the cost and care in handling required.

The water pollution problem from sulfate varies. Several processes (AI, Bergbau, Esso-B and W, IFP, TSK, and Westvaco) have sulfate reduction built into the system. Methods that have thiosulfate in the scrubber circuit (Bureau of Mines, Pfizer, Stauffer, Consol Coal, UOP) have a relatively minor sulfate problem because the thiosulfate inhibits oxidation. The EPA-TVA ammonia process has full oxidation but ammonium sulfate is an acceptable co-product. S and W-Ionics is probably the most vulnerable on this point.

The processes with the most handicap in making sulfur appear to be Bergbau and TSK--because the SO_2 or H_2S is diluted by other gases.

All the second generation methods have the advantage that they are capable of producing elemental sulfur, whereas seven of the 11 first generation processes listed in Table 3 either cannot make sulfur or produce such a dilute SO_2 stream that it would be expensive to do so.

At the present time there is not enough information for a definitive comparison among the second-generation recovery methods. Each has some good points and some drawbacks; the balance can be determined only by further testing. All of them deserve the further support necessary to bring them to the point that an adequate evaluation can be made.

TABLE 1

Second Generation Lime-Limestone Processes

Developer	Absorbent	Principal distinctive feature	Development status
Fuji Kasei (Japan)	Lime	Scrubber type	Full-scale operating
Joy Manufacturing	Lime-limestone	Use of electrostatic precipitator	Pilot
Kellogg	Limestone	Special additive	Pilot
Mitsui Miike (Japan)	Limestone	Oxidation system	Full-scale under construction
National Lime Association	Lime	Rotary drum scrubber	Pilots
TVA	Limestone	Additive (benzoic acid)	Pilot

TABLE 2

Status of Two-Stage Lime-Limestone Processes (Double Alkali)

Developer	Absorbent	Precipitant	Development status
First generation			
A. D. Little	NaOH	$Ca(OH)_2$	Prototype under construction
Chiyoda	Weak H_2SO_4	$CaCO_3$	Full-scale operating
Envirotech	NaOH	$Ca(OH)_2$	Pilot
General Motors	NaOH	$Ca(OH)_2$	Full-scale operating
Kureha-Kawasaki	Na_2SO_3	$CaCO_3$	"
NKK (Japan)	NH_4OH	$Ca(OH)_2$	"
Showa Denko	Na_2SO_3	$CaCO_3$	"
FMC	NaOH	$Ca(OH)_2$	Under construction
Second generation			
Chiyoda (NO_x-SO_2 combination)	Weak H_2SO_4-HNO_3[a]	$CaCO_3$	Pilot
Fuji Kasei	NaOH[a]	$Ca(OH)_2$	Pilot
Kurabo (Japan)	$(NH_4)SO_4$	$Ca(OH)_2$	Pilot
Dowa Mining	$Al_2(SO_4)_3$	$CaCO_3$	Pilot
Lurgi	NaOH	$Ca(OH)_2$	Pilot
Monsanto	Ethanolamine	$Ca(OH)_2$	Pilot
Toyo Engineering	NH_4OH	$Ca(OH)_2$	Pilot

[a] SO_2 and NO_x removal combined.

TABLE 3

Status or Recovery Processes

Developer	Absorbent	Regeneration method	Intermediate	Product	Development status
First generation					
Chemico-Basic	MgO	Thermal	SO_2	H_2SO_4 or S	Full-scale
Grillo	MgO	Thermal	SO_2	H_2SO_4 or S	Prototype
Hitachi	C	None	None	Dilute H_2SO_4	Full-scale
Lurgi	C	None	None	Dilute H_2SO_4	Full-scale
Mitsubishi Heavy Industries	MnO_2	Reaction with NH_3	$Mn_2(SO_4)_3$	$(NH_4)_2SO_4$	Full-scale abandoned
Monsanto	Water	None	None	Concd. H_2SO_4	Full-scale
NIIOGAZ	$(NH_4)_2SO_3$, MgO	Thermal	SO_2	S or H_2SO_4	Full-scale
Shell	CuO	Reduction (H_2)	SO_2	S or H_2SO_4	Full-scale
Sumitomo	C	Thermal	SO_2	H_2SO_4	Full-scale
United Engineers	MgO	Thermal	SO_2	S or H_2SO_4	Full-scale under construction
Wellman-Lord	Na_2SO_3	Thermal	SO_2	S or H_2SO_4	Full-scale

TABLE 3 (Cont'd.)

Developer	Absorbent	Regeneration method	Intermediate	Product	Development status
Second generation					
Atomics International	Na_2CO_3	Reduction (coke)	H_2S	S	Pilot
"	Mixed carbonates	Reduction (coke)	H_2S	S	Prototype
Bergbauforschung	C	Thermal	SO_2	S or H_2SO_4	Prototype
Bureau of Mines	Sodium citrate	Reduction (H_2S)	None	S	Pilot
Consolidation Coal	K_2CO_3 (plus formate)	Reduction (CO)	H_2S	S	Pilot
EPA-TVA	NH_4OH	Acidulation	SO_2	S or H_2SO_4	Pilot
Esso-B and W	CuO	Reduction	SO_2	S or H_2SO_4	Pilot
IFP	NH_4OH	Thermal	SO_2	S	Pilot
Pfizer	Sodium citrate	Reduction (H_2S)	None	S	Pilot
Stauffer	Sodium phosphate	Reduction (H_2S)	None	S	Pilot
S and W-Ionics	NaOH	Electrolysis	SO_2	S or H_2SO_4	Pilot
TSK (Japan)	Na_2CO_3	Reduction (heavy oil)	H_2S	S	Pilot
UOP	Na_2CO_3	Reduction (CO)	H_2S	S	Prototype
Westvaco	C	Reduction (H_2S)	None	S	Pilot

PILOT PLANT TESTING OF THE CITRATE PROCESS FOR SO_2 EMISSION CONTROL

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ABSTRACT

The Bureau of Mines citrate process for removing SO_2 from industrial waste gases comprises absorption of SO_2 in a solution of sodium citrate, citric acid, and sodium thiosulfate followed by reacting the absorbed SO_2 with H_2S to precipitate elemental sulfur and regenerate the citrate solution for recycling. Two pilot plants operated to assess the feasibility of the citrate process for SO_2 emission control have produced tail gas containing less than 50 ppm SO_2 from stack gas containing 1,000 to 5,000 ppm SO_2. A pilot plant constucted by the Bureau of Mines and operated jointly by the Bureau and The Bunker Hill Co. at a lead smelter in Kellogg, Idaho, is described in detail. Nominal capacity of the plant is 1,000 scfm of 0.5-percent SO_2 gas yielding 1/3 ton sulfur per day. General features and operating results are summarized for a pilot plant designed, assembled, and operated by Pfizer, Inc., Arthur G. McKee and Co., and Peabody Engineering to treat 2,000 scfm of 0.1- to 0.2-percent SO_2 gas from a coal-fired steam generating station at Pfizer's Vigo Chemical plant in Terre Haute, Ind. Process economics for coal-fired boiler flue gas desulfurization are projected on the basis of the pilot plant operations.

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PILOT PLANT TESTING OF THE CITRATE PROCESS FOR SO_2 EMISSION CONTROL

INTRODUCTION

Research on techniques for removing SO_2 from waste gases was initiated at the Bureau of Mines Salt Lake City Metallurgy Research Center in 1968. Pioneering research had indicated that effective removal of SO_2 and recovery of sulfur from waste gases might be achieved by absorbing the SO_2 in a suitable solution and then reacting the absorbed SO_2 with gaseous H_2S to precipitate sulfur and regenerate the solution for recycling. After a year of screening many possible reagent combinations of inorganic and organic solutions, we established that a solution of citric acid and sodium citrate was a very effective absorbent for SO_2 and had most of the desirable characteristics that we had been searching for. Among the factors affecting the choice of citrate were chemical stability, low vapor pressure, adequate pH buffering capacity, and the purity and physical character of the precipitated sulfur.

As first studied in the laboratory, the process comprised absorbing SO_2 in citrate solution, reacting the absorbed SO_2 with bottled H_2S, filtering and melting the precipitated sulfur, and recycling the regenerated citrate solution to the SO_2 absorption step. Water produced by the sulfur precipitation reaction was evaporated by the hot gas in the absorption column. Preparation of H_2S from recycle sulfur by reacting sulfur vapor with natural gas and steam over an alumina catalyst was examined separately.

Subsequently a pilot plant to process up to 300 cfm of reverberatory furnace gas was placed into operation in November 1970, jointly by the Bureau of Mines and Magna Copper Co. at the San Manuel smelter in Arizona. Sulfur conversion to H_2S was omitted as being premature. Owing in part to hasty procurement and assembly, intermittent operation of the pilot plant over a 6-month period was troubled by failures of the gas cleaning system, pump breakdowns, and plugging of flow lines by precipitated and melted sulfur. Useful data on consumption of citric acid and other reagents were not obtained, but the SO_2 absorption and regeneration system proved readily manageable for removal of 93 to 99 percent of the SO_2 from the smelter gas. Findings of the initial laboratory and pilot plant research were reported in 1970 and 1971 (_2_, _5_).[1]

The preliminary Bureau of Mines laboratory and pilot plant research demonstrated that the citrate process is capable of substantially complete removal of SO_2 from industrial waste gases. No scaling problems are encountered in the absorber because there are no solids in the clear citrate absorbent liquor. Most of the SO_2 is converted to sulfur with only about 1 percent converted to sulfate regardless of the SO_2 and oxygen content of the feed gas. The process produces an end product of elemental sulfur that can be marketed or readily stored with a minimum of environmental disturbance.

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[1] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

After the encouraging preliminary results, two pilot plant investigations were undertaken to further test the process and obtain useful data for engineering evaluation and cost estimates. This report describes the Bureau of Mines pilot plant operation at The Bunker Hill Co. lead smelter in Kellogg, Idaho, and briefly summarizes the Pfizer-McKee-Peabody pilot plant operation treating stack gas from a coal-fired steam-generating station in Terre Haute, Ind. Estimates of capital and operating costs for removing SO_2 from a 1,000-MW powerplant burning high-sulfur coal also are presented.

PROCESS DESCRIPTION

As a result of further process development in the laboratory leading to an improved method for separating the sulfur from the dilute citrate-sulfur slurry, the citrate process as now envisioned and shown in figure 1 comprises the following steps:

1. The SO_2-bearing gas is cooled to between 45° and 65° C (113° and 149° F) and cleaned of H_2SO_4 mist and solid particles.
2. The SO_2 is absorbed from the cooled and cleaned gas by a solution of sodium citrate, citric acid, and sodium thiosulfate.
3. Absorbed SO_2 is reacted with added H_2S at about 65° C (149° F) and atmospheric pressure, precipitating elemental sulfur, and regenerating the solution for recycle.
4. Sulfur is separated from the solution by oil flotation and melting.
5. The H_2S for step 3, if not otherwise available, is made by reacting two-thirds of the recovered sulfur with natural gas and steam.

CHEMISTRY OF THE PROCESS

Absorption of SO_2 in aqueous solution is pH-dependent, increasing at higher pH. Because dissolution of SO_2 forms bisulfite ion with resultant decrease in pH by the following reaction,

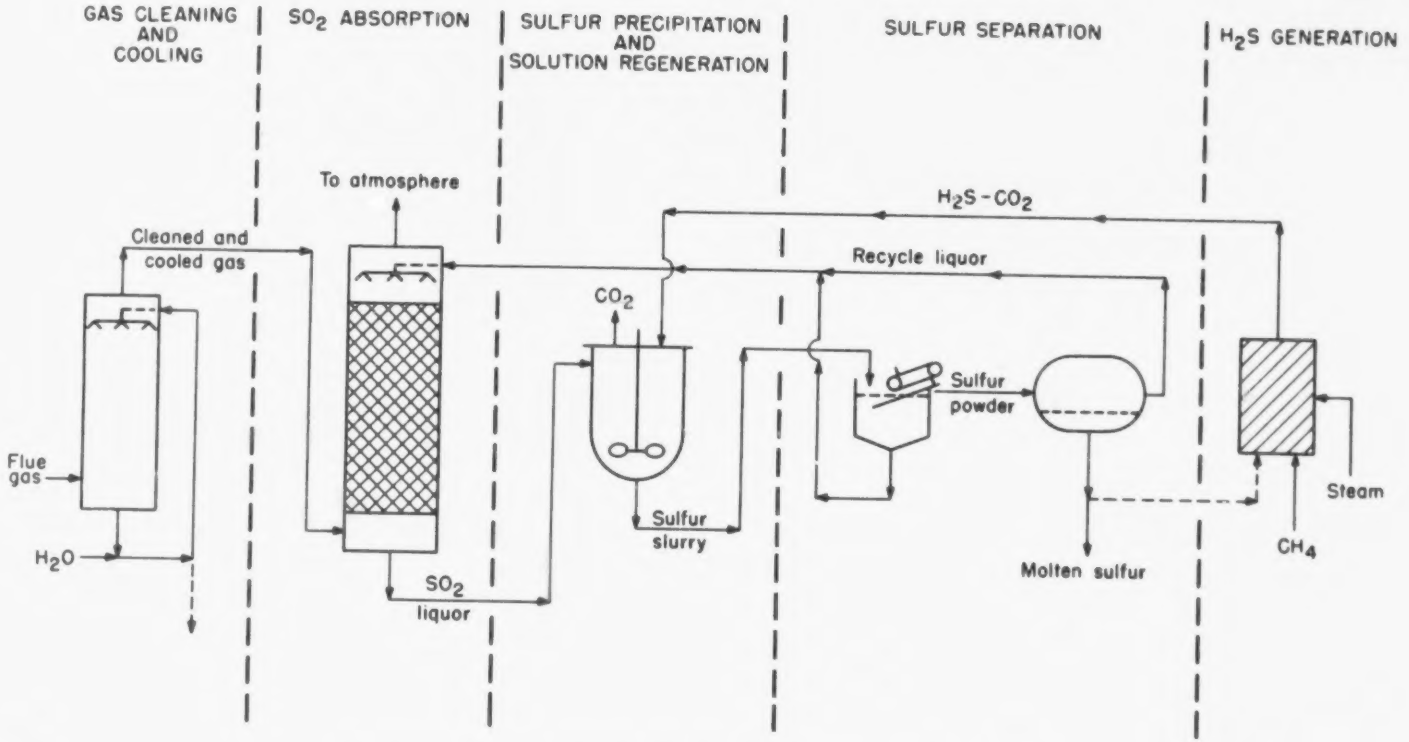

GAS CLEANING AND COOLING
SO$_2$ ABSORPTION
SULFUR PRECIPITATION AND SOLUTION REGENERATION
SULFUR SEPARATION
H$_2$S GENERATION
To atmosphere
Cleaned and cooled gas
Flue gas
H$_2$O
SO$_2$ liquor
CO$_2$
Sulfur slurry
H$_2$S - CO$_2$
Recycle liquor
Sulfur powder
Molten sulfur
Steam
CH$_4$

FIGURE 1.- Generalized citrate process flowsheet.

D-2614-SL

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+, \quad (1)$$

the absorption of SO_2 in aqueous solution is self-limiting. However, by incorporating a buffering agent in the solution to inhibit pH drop, high-SO_2 loadings and substantially complete SO_2 removal from waste gases can be attained. The principal function of the citrate or other carboxylates we have tested is to serve as a buffering agent during SO_2 absorption.

The chemistry is complex for the production of sulfur and regeneration of absorbent by reacting H_2S with the SO_2 in the aqueous solution, but the overall reaction is as follows:

$$SO_2 + 2H_2S \rightarrow 3S^\circ + 2H_2O. \quad (2)$$

Actually, thiosulfate and polythionates are found in solution at equilibrium concentrations after several SO_2-absorption and H_2S-regeneration cycles. Oxidation of SO_2 in the aqueous solution is sharply depressed by complexing of HSO_3^- and H^+ from reaction 1 by the thiosulfate ion, according to the following reaction:

$$H^+ + HSO_3^- + S_2O_3^= \rightleftharpoons (SO_2 \cdot S_2O_3)^= + H_2O. \quad (3)$$

Reaction 3 shows how this complex might react with H_2S to form elemental sulfur and thiosulfate ion.

$$(SO_2 \cdot S_2O_3)^= + 2H_2S \rightleftharpoons 3S^\circ + 2H_2O + S_2O_3^=. \quad (4)$$

To assure satisfactory operation of the system on startup, sodium thiosulfate is added to the initial absorbing solution.

Hydrogen sulfide for regeneration of the absorbent and precipitation of elemental sulfur can be produced by reacting sulfur with methane and steam as shown in reaction 4.

$$CH_4 + 4S + 2H_2O \rightarrow CO_2 + 4H_2S. \quad (5)$$

Other reducing gases such as hydrogen and carbon monoxide can be used in place of methane. More detailed information on the chemistry of the citrate process is provided in a Bureau of Mines publication (6) and a paper presented at the American Chemical Society National Meeting in April of this year (3).

THE BUNKER HILL CITRATE PILOT PLANT

Nominal capacity of the Bunker Hill pilot plant is 1,000 scfm of 0.5 percent SO_2 gas yielding about 1/3 ton of sulfur per day. The plant is to be operated in three phases. Because persistent mechanical failures of the gas cleaning system at the San Manuel copper smelter pilot plant were a principal cause of intermittent operation. Phase I of the Bunker Hill plant operation is designed to treat cleaned, 4- to 5-percent SO_2 gas diverted from the Lurgi sintering furnace feed to the lead smelter acid plant and diluted with air to 0.5 percent SO_2. Commercially produced hydrogen sulfide from a tank trailer is used for the sulfur precipitation reaction. In the Phase II operation, an H_2S generation plant producing 76 to 78 percent H_2S gas by reacting product sulfur with natural gas and steam will replace the nearly pure H_2S from the tank trailer. In Phase III, the lead smelter sinter plant tail gas, which contains dust, acid mist, and from 0.3 to 0.9 percent SO_2, will be used as pilot plant feed. This sinter tail gas presently passes through a baghouse and then is discharged to the atmosphere through Bunker Hill's main stack. In the Phase III operation, in line with conventional lead smelter practice, most of the valuable dust from the tail gas will be recovered in a baghouse, the gas will be cooled in a packed scrubber, and H_2SO_4 mist and traces of particulate matter will be removed by a wet electrostatic precipitator. One of the goals in the test plant operation is to determine the minimum gas cleaning requirement compatible with the citrate process. A block diagram of the complete Bunker Hill pilot plant is shown in figure 2.

Contracts for the design, fabrication, and installation of the Phase I, II, and III plants were awarded to Morrison-Knudsen Co., of Boise, Idaho. Specifications and preliminary design information were provided by the Bureau of Mines. Thio-Pet Chemicals, Ltd., of Calgary, Alberta, Canada, a company with industrial experience in production of hydrogen sulfide and carbon disulfide by the sulfur-methane-steam reaction, acted as subcontractor to Morrison-Knudsen and provided the design for the H_2S generation plant. Construction on the Phase I SO_2 absorption and sulfur recovery plant was completed in early January of this year. After shakedown runs, modifications, and acceptance testing, plant operation began in mid-February. In late September, construction was completed on the H_2S generation plant and pretesting began. Construction is underway on the gas cooling and cleaning plant. This plant is scheduled for completion on January 7, 1975. This report covers the Phase I operation only.

Phase I Plant Description

Figure 3 shows the flowsheet for this phase of the operation. Strong gas containing about 4.5 percent SO_2 from the Bunker Hill Lurgi updraft lead sintering furnace passes through a baghouse, scrubber, and wet electrostatic mist precipitator for removal of particulate matter and H_2SO_4 mist before entering the lead smelter acid plant. Clean acid plant feed gas for the citrate plant is drawn from either of two connections, one between the mist precipitator and the acid plant drying tower and one downstream from the drying tower. This gas is diluted tenfold with air to provide 1,000 scfm of gas containing

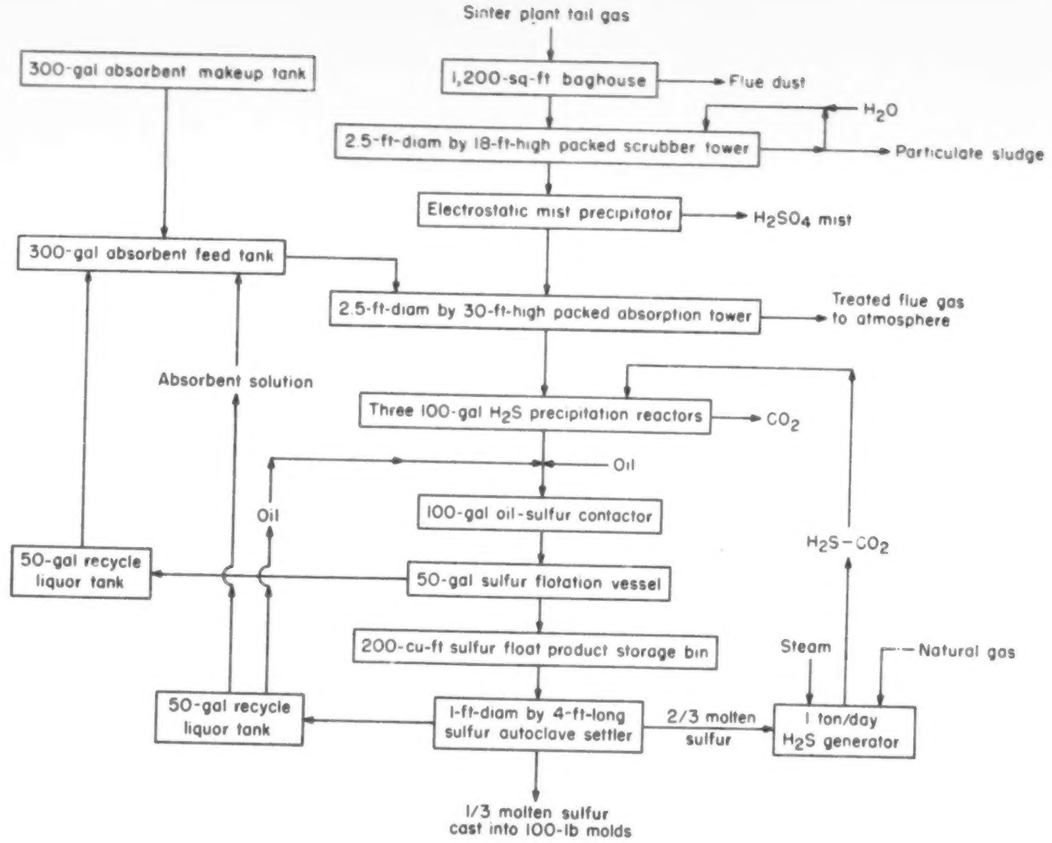
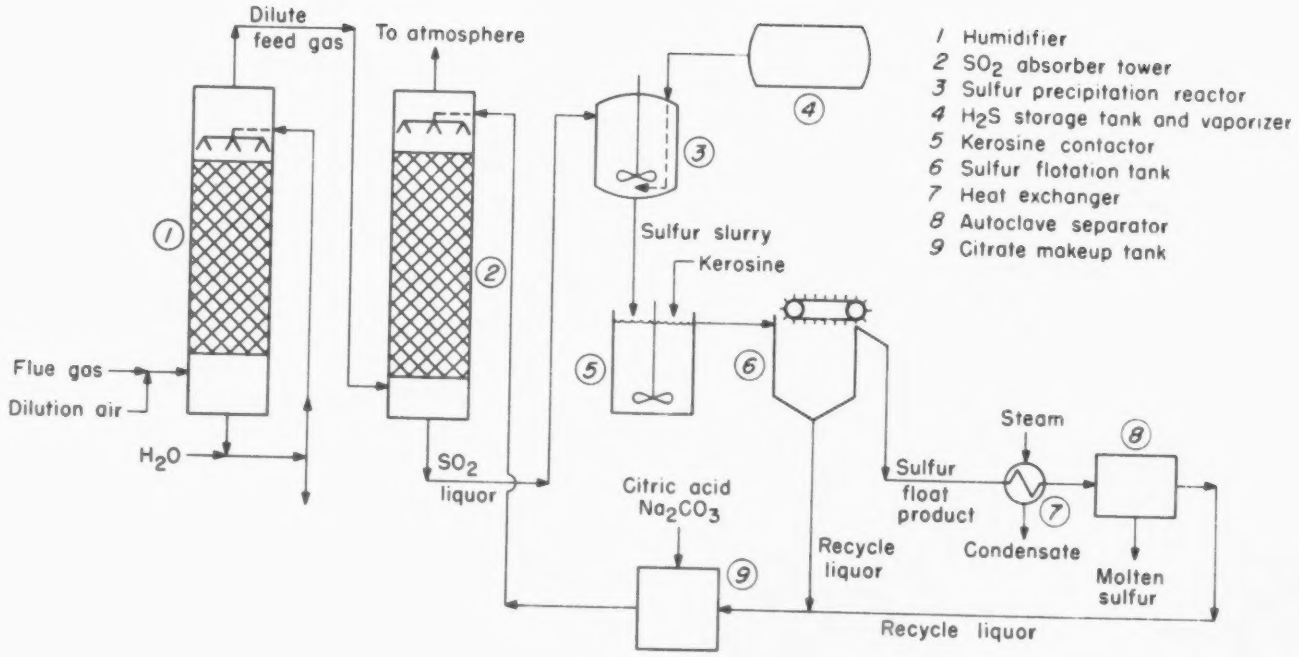

Sinter plant tail gas
1,200-sq-ft baghouse
Flue dust
H_2O
2.5-ft-diam by 18-ft-high packed scrubber tower
Particulate sludge
Electrostatic mist precipitator
H_2SO_4 mist
300-gal absorbent makeup tank
300-gal absorbent feed tank
2.5-ft-diam by 30-ft-high packed absorption tower
Treated flue gas to atmosphere
Absorbent solution
Three 100-gal H_2S precipitation reactors
CO_2
Oil
Oil
100-gal oil-sulfur contactor
H_2S-CO_2
50-gal recycle liquor tank
50-gal sulfur flotation vessel
200-cu-ft sulfur float product storage bin
Steam
Natural gas
50-gal recycle liquor tank
1-ft-diam by 4-ft-long sulfur autoclave settler
2/3 molten sulfur
1 ton/day H_2S generator
1/3 molten sulfur cast into 100-lb molds

FIGURE 2.-Bunker Hill pilot plant.



Dilute
feed gas
To atmosphere
①
②
③
④
⑤
⑥
⑦
⑧
⑨
Flue gas
Dilution air
H_2O
SO_2
liquor
Sulfur slurry
Kerosine
Citric acid
Na_2CO_3
Recycle
liquor
Sulfur
float
product
Steam
Condensate
Molten
sulfur
Recycle liquor
1 Humidifier
2 SO_2 absorber tower
3 Sulfur precipitation reactor
4 H_2S storage tank and vaporizer
5 Kerosine contactor
6 Sulfur flotation tank
7 Heat exchanger
8 Autoclave separator
9 Citrate makeup tank

FIGURE 3.-Bunker Hill citrate pilot plant - Phase I

D-2465-SL

approximately 0.5 percent SO_2. The dilute SO_2 feed gas passes through a 2.5-foot diameter by 18-foot-high Fiberglas-reinforced polyester (FRP) humidifying tower containing a 6-foot section packed with 1-inch polypropylene Intalox[2] saddles and a stainless steel mist eliminator. Humidification of dilution air and the dry gas from the acid plant is required to prevent excessive evaporation of citrate solution in the absorption tower. During humidification, the cool air-gas mixture is heated by steam to raise the temperature of the air. For final temperature control, the diluted gas is heated after humidification to between 45° and 65° C (113° and 149° F) in a steam-to-air heat exchanger with stainless steel tubes. This temperature range corresponds with temperatures to which the lead sintering furnace tail gas would be cooled before treatment in the citrate plant.

The gas stream then is passed upward through a 2.5-foot diameter by 30-foot-high FRP-packed absorption tower countercurrent to the citrate solution, which absorbs over 95 percent of the SO_2. Citrate solution flows through the system at a rate of 10 gallons per minute. The absorption tower contains three 6-foot sections packed with 1-inch polypropylene Intalox saddles and a stainless steel mist eliminator. Other gas-liquid contacting techniques may be applicable, but nearly all our experience in the laboratory has been with packed towers.

From the absorption tower the citrate solution, at a pH of 4.0 to 4.5 and containing about 10 grams SO_2 per liter, flows by gravity to closed stirred vessels for reaction with 2/3 ton of H_2S per day to form 1 ton of elemental sulfur. Three 100-gallon stainless steel reactor vessels arranged for countercurrent flow of citrate solution and H_2S gas are available for the sulfur precipitation step. During the Phase I operation, when nearly pure commercial-grade H_2S is used, the 10-minute retention time available in one reactor usually is sufficient for the sulfur precipitation step. When the H_2S-CO_2 mixed gas prepared from recycled sulfur is used during Phase II operation, three reactors probably will be necessary to insure adequate retention time for contact of the gas and loaded citrate solution. A 1- to 3-percent-solids slurry containing elemental sulfur and regenerated citrate solution overflows the reactors and passes through a common header to a stainless steel reactor effluent tank. From this tank, the dilute slurry is pumped to a 100-gallon FRP conditioner tank where kerosine or other hydrocarbon oil is added for the sulfur flotation-separation step.

The oil-conditioned slurry flows to the 50-gallon-capacity feed well of a specially designed sulfur flotation skimming device. This stainless steel apparatus resembles an Esperanza drag classifier. The sulfur separates from the citrate solution by floating to the surface as a 35- to 45-percent-solids product, leaving clear regenerated citrate for recycle to the absorption tower. A fabric-reinforced, neoprene

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2/ Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

conveyor belt with stainless steel flights skims sulfur off the surface of the citrate solution in the feed well. The sulfur is pulled up an inclined chute and is discharged to a 200-cubic-foot, stainless steel conical storage bin.

Regenerated citrate solution from the feed well of the sulfur skimmer passes through a 50-gallon FRP settling tank and then to a 300-gallon FRP absorber feed tank. Any sulfur solids carried over to the settler from the sulfur flotation skimmer are periodically pumped back to the oil-conditioning tank with a diaphragm pump. Citrate solution from the absorber feed tank is pumped through parallel backwash clarification filters and a water-cooled heat exchanger to the absorption tower.

On day shift only, the sulfur float product is withdrawn from the storage bin with the aid of an attached vibrator and pumped by a Moyno positive displacement auger-type pump through a single-tube, steam-jacketed heat exchanger where the sulfur is melted at about 135° C (275° F). Molten sulfur and citrate solution pass into a closed settler tank at 135° C and under a pressure of 35 psi. Molten sulfur is tapped from the bottom of the autoclave settler and cast in 100-pound blocks. During the Phase II operation, a bleed stream of molten sulfur will flow to the H_2S generating plant. Citrate solution and the oil used for flotation are withdrawn from the top of the settler through a sulfur knockout pot, filter, and water-cooled heat exchanger into a 50-gallon FRP decanting vessel for separation and reuse. Citrate solution from this tank drains to the absorber feed tank.

Materials of construction used in the Bunker Hill pilot plant were chosen to resist corrosion by the SO_2 gas and citrate liquor process streams. Process piping is stainless steel, FRP, polyvinyl chloride (PVC), or chlorinated polyvinyl chloride (CPVC), as applicable. All stainless steel in the plant is type 316. An H_2S incinerator is provided outside the main building to burn H_2S vented from the sulfur precipitation reactors, oil flotation conditioner, and H_2S tank trailer areas, and to incinerate gas released under emergency or upset conditions. The small amount of strong SO_2 gas from the incinerator passes through a duct to the main baghouse of The Bunker Hill Co. lead smelter where it is diluted by the nearly 200,000 cfm of gas from the lead blast furnaces going up the main stack. A 40-foot-long van modified to serve as a laboratory and instrument trailer is connected to the main building. The pilot plant is completely instrumented and controlled from the panel in the instrument trailer. A paper providing more detail on the design of the Bunker Hill pilot plant was presented at the 1974 AIME Annual Meeting in Dallas, Tex. (4).

Phase I Plant Operating Results

Phase I operation of the Bunker Hill citrate pilot plant was started on February 13, 1974. The plant has operated for a total of 1,300 hours through August 29, producing about 45 tons of bright yellow, high-quality sulfur. Because of interruptions resulting from changing work crews, mechanical failures, and unavailability of feed gas, the longest continuous operation to date has been about 160 hours. Citrate loss over this period was 7.5 pounds per net long ton of sulfur recovered from feed gas. Sulfur dioxide removal from feed gas containing 0.3 to 0.45 percent SO_2 ranged from 93 to 99 percent when operating at the design gas flow rate while varying gas temperature and citrate concentration. Regeneration of the citrate solution and precipitation of sulfur with H_2S has been easily controlled in a single reactor. The precipitated sulfur has been successfully recovered as a high-purity product by oil flotation and melting.

Table 1 summarizes results obtained under reasonably steady-state continuous operation at gas flow rates of 1,000 and 1,250 scfm and SO_2 concentrations of 0.3 to 0.45 percent. Gas temperatures ranged from 35° to 50° C (95° to 122° F). Citrate solution concentration was 0.5 M for most of the tests, the sodium-to-citric acid molar ratio in the citrate solution was 2:1, and the pH of the citrate feed solution to the absorption tower was about 4.5.

TABLE 1. - Results of Bunker Hill citrate pilot plant operation - February to September 1974

Gas flow rate, scfm	Feed gas concentration, pct SO_2	Gas temperature, ° F	Citrate solution flow, gal/min	Citrate solution loading, g/l SO_2	Off-gas, ppm SO_2	SO_2 removal, pct
1,000	0.32	95	[1]10	6.3	32	99.0
1,000	.41	100	[1]10	8.8	57	98.6
1,000	.34	116	10	6.7	190	94.4
1,000	.44	122	10	8.9	300	93.2
1,000	.45	109	8	10.2	70	98.4
1,250	.42	119	10	9.9	340	91.9

[1] 0.25 M citrate solution.

The test results show that at the design flow rate of 1,000 scfm, SO_2 absorption decreased from 99 percent at a gas temperature of 35° C (95° F) to 93 percent when the gas temperature was 50° C (122° F). Exit gas from the pilot plant ranged from 300 ppm SO_2 at the higher temperature to only 32 ppm at a gas temperature of 95° F. Excellent SO_2 absorption was obtained with the more dilute citrate solution at the lower temperatures, even though the solution loading represents

65 percent of the maximum equilibrium loading of the 0.25 M citrate solution as compared with about 55 percent of the maximum loading for the 0.5 M absorbent liquor.

The SO_2 removal efficiency was still over 98 percent, and the offgas contained less than 100 ppm SO_2 when the citrate solution flow rate was decreased to 8 gallons per minute, thus increasing the loading to 10 grams SO_2 per liter. This loading represents 60 to 65 percent of the maximum equilibrium loading of 0.5 M citrate solution at the test temperature of 109° F. In the test made at a gas flow rate of 1,250 scfm at the higher temperature of 119° F and operating with the higher SO_2 loading of the citrate liquor, the SO_2 content of the offgas increased to 340 ppm, but the SO_2 removal efficiency still exceeded 90 percent.

At the design capacity of the plant, a gas flow rate of 1,000 scfm and a solution flow rate of 10 gallons per minute, the total pressure drop through the absorption tower was 6 inches of water. As the solution flow rate was reduced to 8 gallons per minute to increase the SO_2 loading of the citrate solution, the pressure drop decreased to 5.6 inches of water. Operation of the plant at a gas flow of 1,250 scfm with 10 gallons per minute of citrate solution flowing through the absorption tower increased the pressure drop to 9 inches of water.

Precipitation of sulfur with commercially produced, nearly pure H_2S and regeneration of the citrate solution for continued absorption took place in a single reactor. No sulfur buildup occurred along the walls of the stainless steel reactor or on the impellor provided the tip speed of the impellor was at least 900 feet per minute. In the early stages of plant operation, excess H_2S absorbed in the citrate solution resulted in cloudy recycle solution recovered from the kerosine flotation step, apparently due to delayed precipitation of colloidal sulfur. In addition, some of this absorbed H_2S escaped at times from the sulfur skimmer into the plant building. This problem was corrected by using a second stirred reactor as a delay tank to allow more contact time with the H_2S and bypassing about 5-volume percent of the SO_2-loaded liquor from the absorption tower to the reactor effluent tank to react with the excess absorbed H_2S. These measures have resulted in consistently clear citrate solution from sulfur flotation for recycling to the absorption tower and have stopped the escape of H_2S from the sulfur flotation equipment.

No problems have been encountered in plugging of lines between reactors and the reactor effluent tank. A problem existed with sulfur buildup in the automatic level-controlled reactor effluent tank until a small agitator was installed to keep the sulfur in suspension. The kerosine conditioner tank operates well with no sulfur buildup at the design liquid flow rate, provided the impellor tip speed is at least 700 feet per minute. Some trouble was experienced initially with holdup of floated sulfur in the freeboard of the tank necessitating occasional cleanout of the 3-inch-diameter overflow line to the skimmer. However, the addition of a second impellor operating just beneath the liquid surface prevented buildup of the large lumps of powdery floated sulfur that were blocking the overflow line.

A powder-like sulfur product of about 50 percent solids has been obtained by adding between 35 and 40 pounds of kerosine per ton of sulfur produced. About 20 percent of the kerosine added for flotation has been recovered from the melting operating for reuse. Most of the kerosine loss can be attributed to volatilization from the hot sulfur slurry in the kerosine conditioner and sulfur skimmer. Because of this high volatilization loss, kerosine consumption during the pilot plant operation to date has averaged 90 pounds per net ton of sulfur recovered from the feed gas. Laboratory tests have indicated that this hydrocarbon consumption can be reduced considerably by using low-volatile motor oil in place of kerosine. In a 20-scfm continuous test plant at the Salt Lake City Metallurgy Research Center, the use of SAE 10 motor oil resulted in a sulfur float product equivalent to that produced with kerosine, and the oil consumption was one-fourth that of kerosine. Various oils will be investigated in future campaigns at the Bunker Hill pilot plant.

The sulfur melting step has functioned satisfactorily at the design capacity. The melting rate seems to be limited to about 300 pounds of sulfur per hour by the maximum speed of the drive mechanism on the Moyno sulfur pump. Some plugging problems have been encountered in the citrate liquid lines from the autoclave settler, apparently because of sulfur being dissolved in the kerosine flotation reagent and then crystallizing out upon cooling. Possibly, a dual filter downstream of the liquid cooler or substitution of motor oil for kerosine will solve this problem.

The sulfur produced by the Bunker Hill citrate pilot plant has been bright yellow and of better than 99.5-percent purity. Carbon content has ranged from 0.2 to 0.3 percent. In the laboratory, continuous test plant sulfur recovered by motor oil flotation contained 0.01 percent carbon.

During operation of the Bunker Hill citrate pilot plant, the rate of oxidation of SO_2 to $SO_4^=$ was determined to be about 1.3 percent. This is quite low considering that the feed gas, which is predominately air, contained about 20 percent O_2. Since the plant was started up in February, the thiosulfate concentration of the citrate solution has ranged from 20 to 40 grams per liter. The sulfate concentration has built up to about 40 grams per liter. However, this figure is not representative of the greater sulfate buildup expected because of a few plant upsets resulting in large solution losses, which required a makeup of fresh citrate solution. These losses occurred when the reactor effluent tank or kerosine conditioner tank plugged causing citrate solution to back up and flow through vent lines to the H_2S incinerator. These large solution losses appear to have been eliminated by the modifications to the reactor effluent tank and kerosine conditioner. In addition, large collection tanks have been installed in the vent lines to the incinerator should plugging problems occur again.

In Phase II of the Bunker Hill pilot plant operation, the H_2S generation plant will be operated utilizing both a one-stage and two-stage procedure for production of H_2S by the sulfur-methane-steam reaction to provide data for engineering evaluation of this important step in the citrate process. The H_2S generation plant also will be operated in conjunction with the sulfur dioxide absorption and sulfur recovery section to determine the influence of the impure H_2S gas on sulfur precipitation and SO_2 removal efficiency.

In addition to operating the gas cooling and cleaning plant to determine gas cleaning requirements during Phase III operation of the pilot plant, test campaigns will be run on the Lurgi sinter furnace tail gas to further relate feed gas temperature, citrate concentration, and citrate solution loading to SO_2 absorption.

THE TERRE HAUTE CITRATE PILOT PLANT

The Pfizer-McKee-Peabody citrate pilot plant at Terre Haute, Ind., is described in two recent publications (1, 3). Briefly, the skid-mounted unit treated 2,000-scfm of gas from a coal-fired spreader stoker-type boiler with a 25,000-pound per hour steam-rated capacity. The flue gas was adiabatically cooled with quench water and passed into a Venturi-type water scrubber to remove fly ash. Absorption of SO_2 took place in an impingement plate scrubbing tower using an aqueous solution of sodium citrate and citric acid. The SO_2-rich citrate solution flowed from the absorber through a steam-heated heat exchanger to a three-stage continuous stirred tank reactor system countercurrent to a flow of pure H_2S from a tank trailer. The SO_2 was reduced to sulfur and the citrate solution regenerated. Sulfur slurry was pumped from the reactors to a surge tank and then to a sulfur flotation separation system. Citrate liquor was recycled from the flotation unit to the absorption system. The sulfur flotation product was pumped as a slurry through a heater at a temperature above 125° C (257° F) and a pressure of 70 psig to melt the sulfur. Liquid phases were separated in a pressure decanter where the bottom layer was drawn off as high-quality molten yellow sulfur and the citrate solution top layer was discharged to a flash drum at reduced pressure.

The following statement on plant operation was furnished by Louis Korosy of Pfizer Inc., Frank Chalmers of Arthur G. McKee and Co., and Srini Vasan of Peabody Engineering Systems:

"While generally similar to the Bureau of Mines unit, there are two major design differences in the Terre Haute plant: (1) An impingement plate tower is used rather than a packed tower. This permits the use of higher gas velocities and thus smaller tower diameters; (2) the sulfur separation is based on a flotation principle, but no hydrocarbon addition is made.

Operation under the final equipment configuration started on March 15. Between then and September 1, 2,330 hours of operation were logged. Runs were generally five to six days in length.

During this period the SO_2 removal efficiency of the system was well above 95 percent. SO_2 in the exit gas consistently was less than 50 ppm and actually averaged 34 ppm. At this time the inlet gas to the system averaged about 1,000 ppm SO_2.

The trouble-free operation of the absorber in the citrate process was highlighted during one phase of the pilot plant program. While clear liquor is normally returned to the absorber from the surfur separation step, for a period of weeks sulfur slurry was deliberately returned to the absorber. No problems were encountered.

At this point the test unit has provided sufficient data to prepare scale-up designs for further projects on a guaranteed SO_2 removal basis."

COST ESTIMATE FOR CITRATE PLANT AT COAL-BURNING POWERPLANT

Based on results of the Bunker Hill and Terre Haute pilot plant operations, a cost estimate was prepared by the Process Evaluation Group at the Salt Lake City Metallurgy Research Center to determine the cost of removing 95 percent of the sulfur from the tail gas of a 1,000-MW coal-burning powerplant. Assuming that the powerplant burns 8,400 tons per day of coal containing 3 percent S, the gas flow would be 1,730,000 scfm (60° F) with an SO_2 content of 0.24 percent. The yield of sulfur would be about 214 long tons per day. The plant is assumed to operate 7,000 hours (292 days) per year.

Annual operating costs for the plant are itemized in table 2. A summary of operating labor requirements, fixed capital cost, annual operating costs, and unit production costs for each of the unit operations and for the entire plant are presented in table 3. The fixed capital costs were estimated by standard chemical engineering cost estimating procedures for a "study estimate" and are for the second quarter of 1974 or a Marshall and Swift (M&S) index of 386.

The operating cost of the citrate plant includes reheating the final tail gas from 50° to 170° C (122° to 340° F) with a natural gas burner at the base of the powerplant stack. Operating losses are assumed at 11.2 pounds of citric acid and 16 gallons of kerosine per long ton of product sulfur. Costs for Na_2SO_4 removal were estimated on the basis of 1 percent of the removed sulfur being converted to sulfate.

TABLE 2. - Annual operating cost of SO_2 removal from 1,000-MW powerplant offgas

	Unit cost	Total cost
Direct cost		
Raw materials		
Citric acid	$349,100	
Soda ash	48,600	
Kerosine	648,400	
		$1,046,100
Utilities		
Electricity	317,600	
Natural gas	2,546,000	
Process water	13,900	
Cooling water	223,700	
Steam	941,600	
		4,042,800
Direct labor		
Labor	151,500	
Supervision	22,700	
		174,200
Plant maintenance		
Labor	563,900	
Supervision	112,800	
Materials	655,800	
		1,332.500
Payroll overhead		212,800
Operating supplies		266,500
Total direct cost		7,074,900
Indirect cost (administration and overhead)		709,300
Total capital charges		6,084,800
Total annual operating cost		13,869,000

TABLE 3. - Summary of costs for SO_2 removal from a 1,000-MW powerplant offgas

	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Gas cooling and SO_2 absorption	4.2	$19,951,000	$8,096,000	$129.86
Sulfur precipitation	2.1	611,000	1,183,000	18.98
Sulfur recovery	2.1	3,217,000	1,680,000	26.95
H_2S generation	2.3	3,056,000	2,685,000	43.06
Na_2SO_4 removal	2.3	483,000	225,000	3.61
Facilities	-	2,714,000	-	-
Utilities	-	3,257,000		
Fixed capital	-	33,289,000	-	-
Working capital	-	3,100,000	-	-
Total	13.0	36,389,000	13,869,000	222.46

Direct costs include materials and utilities at the following unit costs: Citric acid at $1,000 per ton; soda ash at $40 per ton; kerosine at $0.65 per gallon; electric power at $0.01 per kW-hr; natural gas at $1.00 per thousand cubic feet; and water at $0.17 per thousand gallons for process use, and $0.03 per thousand gallons for cooling. These costs also include direct labor at $5.60 per hour, plus supervision at 15 percent of direct labor; plant maintenance consisting of maintenance labor at 2.2 percent of fixed capital costs, plus supervision at 20 percent of maintenance labor and maintenance material at 116 percent of maintenance labor; payroll overhead at 25 percent of the cost of labor and supervision for operations and maintenance; and operating supplies at 20 percent of plant maintenance.

Indirect costs are 40 percent of direct labor, plant maintenance, and operating supplies.

Capital charges, which include amortization, taxes, and insurance are 17 percent of the total capital which is the average annual fixed capital charge for privately financed steam-electric plants.

As shown in table 3, the capital investment for a citrate plant at a 1,000-MW coal-burning powerplant is estimated at $36.4 million. Assuming no credit for sulfur, operating cost for removing 95 percent of the SO_2 from the stack gas is about $13.9 million. This is equivalent to $5.66 per short ton of coal or 1.98 mills per kW-hr.

FUTURE PLANS

Plans are underway for one or more large-scale plants to demonstrate the citrate process for SO_2 emission control at powerplants or steam-generating facilities burning high-sulfur coal or oil. The demonstration plants will operate on 30- to 60-MW powerplants or steam-generating plants of equivalent capacity. They will be provided and operated under a cooperative arrangement and cost sharing basis between the Bureau of Mines and the Environmental Protection Agency and interested industrial firms. Proposals for demonstration plants including preliminary engineering estimates are to be submitted by early December 1974. Contracts will be awarded, after negotiations, probably early in 1975.

Work on the citrate demonstration plant contracts will be divided into four phases. Phase I, consisting of process design and definitive cost estimates, should be completed by July 1975. Phase II, which includes detailed engineering design, construction, and mechanical acceptance of the plants, should be completed by July 1978. Phase III consisting of startup and performance acceptance testing would take place at the conclusion of Phase II. This would be followed by Phase IV, comprehensive emission testing programs to be conducted at the demonstration plants by independent contractors for 1 year.

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TVA-EPA PILOT-PLANT STUDY OF THE AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PROCESS

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ABSTRACT

The Tennessee Valley Authority and the Environmental Protection Agency began studies of an ammonia scrubbing program at TVA's Colbert pilot plant in 1969. The principal advantage in the TVA-EPA process is economic regeneration by acidulation with ammonium bisulfate produced from thermal decomposition of ammonium sulfate. This paper highlights the pilot-plant activities since the 1973 Flue Gas Desulfurization Symposium.

Absorber product liquors, that are amenable to regeneration, have been produced while obtaining good SO_2 removal and low ammonia losses. However, the following problem areas have been established:

- Open-loop operation of the prewash section.
- Fume formation in the absorber and after discharge from the stack.
- Solids precipitation in the absorber liquors.
- Incomplete SO_2 release in the acidulation and stripping operations.

The prewash section was operated open loop to minimize corrosion but will have to be closed in a final process design. Under proper operation of the system, it is possible to control fume formation inside the absorber while operating at relatively high salt concentrations. Avoiding fume formation on days of low temperature and high relative humidity may be impractical to achieve. Precipitated solids in the absorber liquor may present problems in the regeneration section. Most of the absorbed SO_2 can be released in the acidulator and stripper, but the remaining SO_2 creates problems in the evaporator. The acidulator and stripper are being redesigned to achieve a complete release of SO_2. An ammonium sulfate decomposer has been designed.

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TVA-EPA PILOT-PLANT STUDY OF THE AMMONIA ABSORPTION -
AMMONIUM BISULFATE REGENERATION PROCESS

Absorption of sulfur dioxide from plant flue gases using ammoniacal solution and subsequent regeneration of the absorbing solution has been proposed or demonstrated in several processes. Lepsoe and Kirkpatrick[1] report that one of the earliest of these is the Cominco process in which SO_2 from a smelter operation is absorbed in an ammoniacal solution, the solution is acidulated to produce ammonium sulfate for disposal as a fertilizer and the evolved SO_2 is sent to an acid plant. TVA piloted a similar process on power plant stack gases in the 1950's according to Hein, et al.[2] Other processes which produce fertilizers as the end product have been developed and are in full-scale operation on sulfuric acid plant tail gases in Czechoslovakia and Romania.[3,4] These processes use nitric or phosphoric acid to release the SO_2 and produce marketable fertilizers. Limited long-term markets for ammonium sulfate and the constraints on the location of power plants to fertilizer manufacturing centers limit their usage in the U.S.

Regeneration processes that do not rely on fertilizer marketing have been studied extensively. H. F. Johnstone[5] developed a process in the 1930's that produced only SO_2. Steam stripping was employed to recover SO_2 and to regenerate the ammoniacal solution for reuse in the scrubber. Since concentrated SO_2 is the major product, either sulfuric acid, liquid SO_2, or elemental sulfur can be the final product, depending on the need of the user. Although the Johnstone process has been operated successfully on a small pilot scale and presupposes no link to a fertilizer plant, it possesses some undesirable characteristics. Energy requirements for the stripping step are relatively high, 10-15 pounds of steam per pound SO_2. Oxidation products are difficult to purge from the system without loss of active species as well. The occurrence of undesirable disproportionation reactions in the steam stripper further aggravates the oxidation problem.

Development of the Johnstone process has been vigorously pursued in the USSR. Several pilot-plant studies led to installation of a large-scale (about 70 MW) system on a coal-fired power plant in Moscow in 1952 and the system was operated until the power plant was converted to burn gas in 1961. Regeneration was based on steam stripping. A wet electrostatic precipitator was reported effective in controlling fume emission. During the period 1968-1972, an ammonia scrubbing process was used on a 15-megawatt oil-fired power plant located at Ufa in the Ural Mountains. Both direct oxidation to produce ammonium sulfate and regeneration by the autoclave process were tested. Corrosion was a serious problem.

Design work has been started on an ammonia scrubbing system for a full-scale (about 250 MW) oil-fired boiler near Moscow. Completion in 1977 is planned. Thermal regeneration will be used for recovery of SO_2, but the TVA-EPA ammonium bisulfate process is also being considered. Ammonia scrubbing is included in the agreement for formal exchange of technology between the U.S. and the USSR.

Other regenerative schemes not dependent on the fertilizer market structure are mentioned below.

The Institut Francais de Petrole (IFP) in France is developing a process based on ammonia scrubbing. The various steps of the process have been piloted separately at various locations. Two intergrated systems are now being installed in Japan; one on a Claus plant and one at a refinery.

In March 1974, Nippon Kokan KK began operating a full-scale ammonia/lime double-alkali unit for treating 150,000 Nm^3/h waste gas from an iron ore sintering plant (300,000 Nm^3/h capacity) at the Keihin Works, Kawasaki, Japan. An ammonia-based fume from the absorber is considered a major problem. The calcium salts in the system are converted to gypsum and discarded. No additional units are currently being installed by Nippon Kokan KK using the ammonia double-alkali scrubbing process.

In September 1973, TVA modified its limestone - wet-scrubbing pilot plant to obtain preliminary data on an ammonia-limestone/lime (double alkali) scrubbing process. Good SO_2 removal was obtained (90% +). Two major problems identified during the initial period of this pilot-plant operation were (1) excessive losses of soluble ammonia-sulfur salts with the discarded solids (calcium sulfite, fly ash, and unreacted limestone) from the filtration step and (2) formation of a dense, persistent plume by the scrubbed gases exhausted to the atmosphere.

THE TVA-EPA AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PROCESS

In 1968, EPA contracted with TVA to begin a pilot-plant program to study in depth the ammonia absorption process as applied to power plants. The pilot plant was located at TVA's Colbert Power Plant, a pulverized coal-fired installation in northwest Alabama. The initial phase of study covered a number of variables in the absorption step. The results led EPA and TVA to amend the program to include a process for regenerating the liquor from the absorber operation. Both TVA and EPA have shared in funding the amended study. The regeneration process selected for the second phase of pilot-plant study was the ammonium bisulfate process. A topical report recently issued by TVA[6] and a paper given at the Flue Gas Desulfurization Symposium in New Orleans by Hollinden, et al.,[7] last year covers the early absorption study and the first year's work on the regeneration process. The purpose of this paper is to update those reports to cover the past year's pilot-plant work.

The TVA-EPA ammonium bisulfate regeneration process (ABS process) uses a version of the Hixon-Miller[8] scheme for release of SO_2 from ammoniacal solutions by acidification and subsequent decomposition of the ammonium sulfate product to ammonia for recycling to the absorber and ammonium bisulfate for recycling to the acidulator. The net absorption reactions are:

(1) $NH_3 + SO_2 + H_2O \longrightarrow NH_4HSO_3$
(2) $NH_4HSO_3 + NH_3 \longrightarrow (NH_4)_2SO_3$
(3) $(NH_4)_2SO_3 + SO_2 + H_2O \longrightarrow 2NH_4HSO_3$

The net regeneration reactions are:

(4) $NH_4HSO_3 + NH_4HSO_4 \longrightarrow (NH_4)_2SO_4 + H_2O + SO_2\uparrow$
(5) $(NH_4)_2SO_3 + 2NH_4HSO_4 \longrightarrow 2(NH_4)_2SO_4 + H_2O + SO_2\uparrow$
(6) $(NH_4)_2SO_4 \xrightarrow[\Delta]{700°F} NH_4HSO_4 + NH_3\uparrow$

As in the Johnstone process, the only product from the ABS process is a gaseous stream of SO_2. The ABS process has advantages over the sulfite steam stripping process in that disproportionation reactions are avoided and sulfites are not purged from the system. Also, energy requirements for the ABS process are estimated to be approximately one-half to two-thirds that of the Johnstone process. For simplicity, the pilot plant is divided into the absorption and the regeneration sections.

Absorption Section

A flowsheet of the absorption section of the pilot plant is shown in Figure 1. The pilot plant is designed to treat approximately 3000 cfm of flue gas at absorber conditions (saturated at about 125°F). The gas flows through a prewash section containing a venturi-type element. The conditioned gas is then routed to the absorption tower. The absorber consists of as many as four independent absorbing stages (valve tray elements).

The makeup water to the absorber is added to the top recirculating stage (G-4) to maintain a low salt concentration at the top of the tower to control the ammonia loss from the system. Ammonia is added to the second absorption stage (G-2). A portion of the liquor from the bottom tray is pumped to G-2 to decrease the pH of the liquor on the second stage. Decreasing the pH reduces the vapor pressure of ammonia which decreases the possibility of gas phase reactions of ammonia, SO_2, and water to form a fume in the absorber. Product liquor is withdrawn from the first stage (G-1) and is stored in surge tanks for use in the regeneration section. The scrubbed flue gas is exhausted to the atmosphere either with or without reheating.

A discussion of the individual steps follows:

Gas Pretreatment. The inlet flue gas enters the pretreatment section (Figure 2) through a 1- by 1-foot duct which contains a venturi

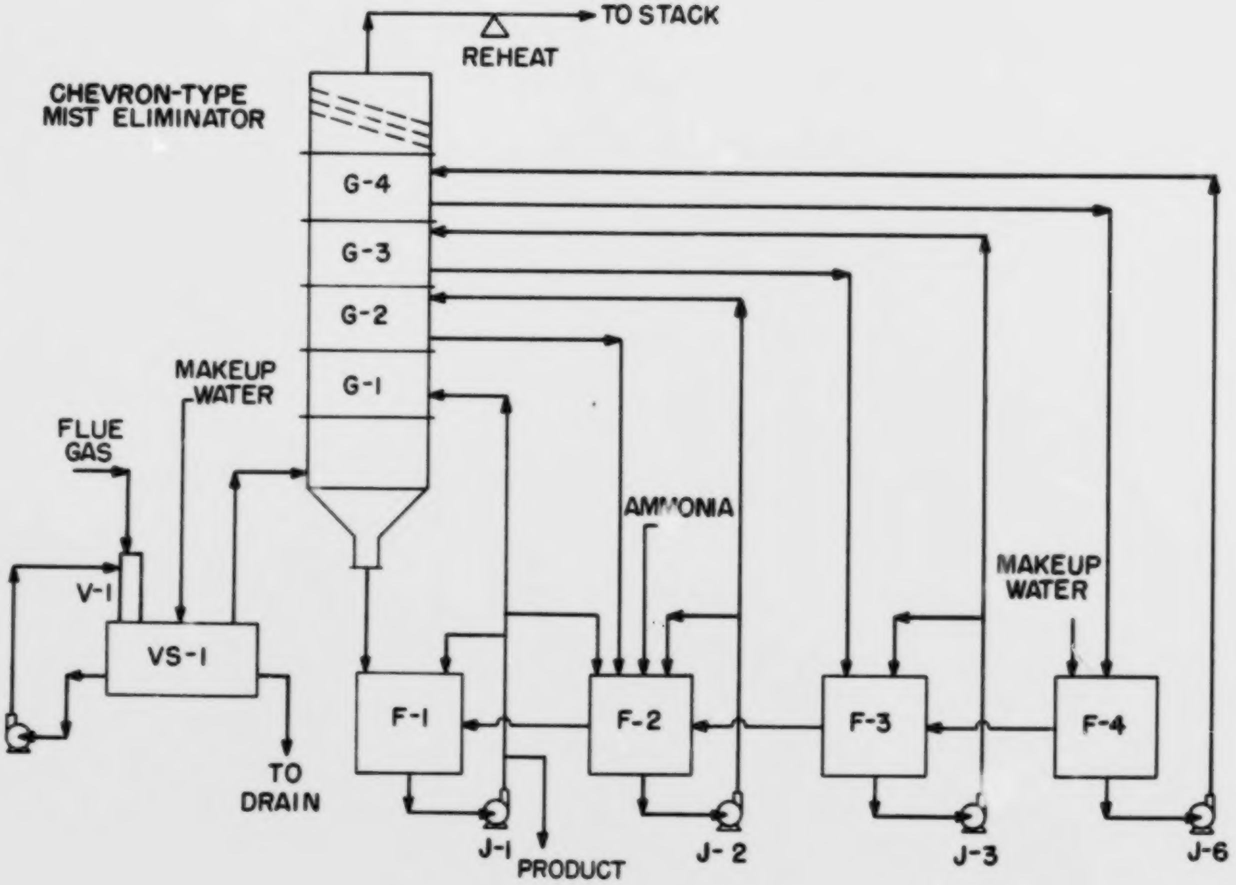
TO STACK
REHEAT
CHEVRON-TYPE MIST ELIMINATOR
G-4
G-3
G-2
G-1
MAKEUP WATER
FLUE GAS
V-1
VS-1
TO DRAIN
AMMONIA
MAKEUP WATER
F-1
F-2
F-3
F-4
J-1
PRODUCT
J-2
J-3
J-6

Figure 1. Absorption section.

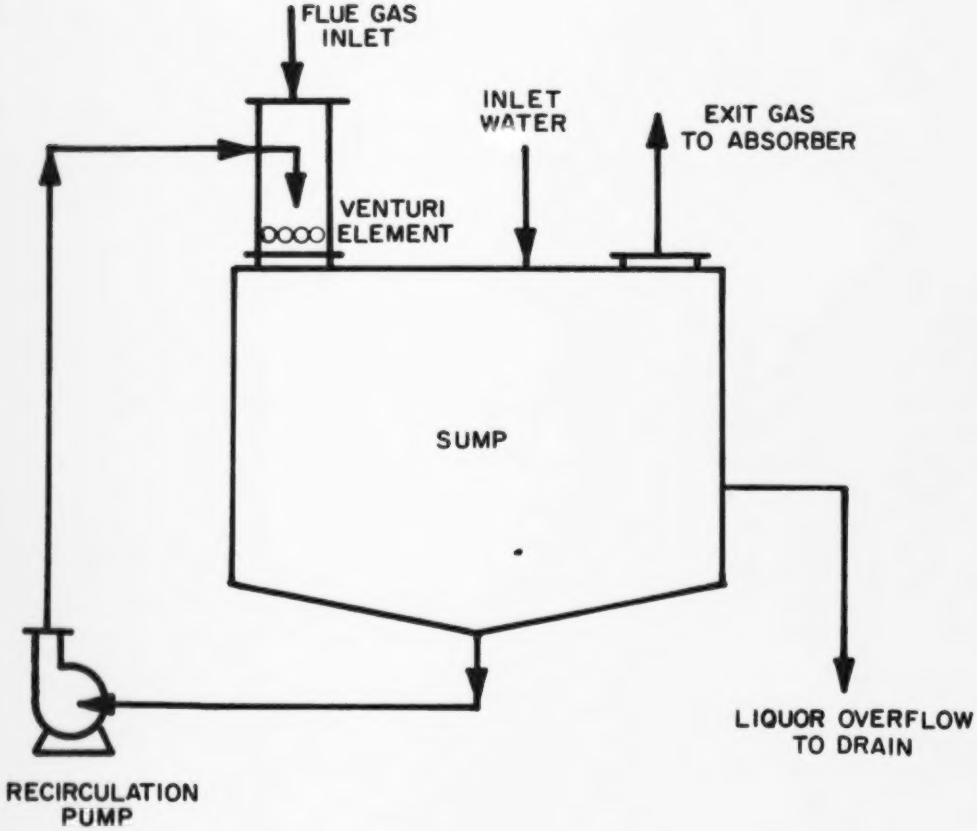
FLUE GAS INLET
INLET WATER
EXIT GAS TO ABSORBER
VENTURI ELEMENT
SUMP
LIQUOR OVERFLOW TO DRAIN
RECIRCULATION PUMP

Figure 2. Prewash section.

element similar to Environeering Inc.'s Ventri-Rod element. The element consists of a number of 3/4-inch rods mounted perpendicular to the gas flow. The number of rods can be varied to increase or decrease the pressure drop (ΔP) across the element. Recirculating wash water from a sump beneath the venturi element is sprayed cocurrently with the gas stream immediately upstream from the element.

The gas and spray water passes through the venturi element and into the sump. The velocity of the flue gas decreases in the sump to 8 feet per second allowing some of the spray water entrained in the venturi to separate. The gas travels the length of the sump and is routed through a 14-inch-diameter duct to the absorber.

The purpose of the gas pretreatment is to humidify and cool the flue gas and to remove fly ash and chlorides from the gas stream. Humidification, cooling, and chloride removal are considered necessary for reducing the plume emission from the absorber. Fly ash is removed before the absorption section to decrease the amount of solids in the scrubber liquor. These solids could cause major problems in the absorption and regeneration sections.

In the test program, the pressure drop across the venturi and the liquid-to-gas ratio (L/G, gal/1000 ft^3) of wash water to the element were varied to determine their effects on the particulate, sulfur dioxide, and chloride removal, and on mist carryover. The pressure drop ranged from 0.5 to 15.0 inches of water and the L/G from 10 to 30. The flue gas used was taken both upstream and downstream from an electrostatic precipitator. The results of these tests are summarized below.

- The inlet fly ash loading was reduced an average of 93% when the inlet dust loading was 4 to 6 grains of dust per dscf. No reduction in dust loading was obtained when the inlet loading was low (0.01-0.1 gr/dscf).

- No direct relationship was established between the SO_2 removal and the L/G, pressure drop, or pH of the wash water in the prewash section. Between 7 and 23% of the inlet SO_2 (2600 ppm) was removed in the section.

- An increase in the pressure drop across the venturi element and the L/G to the element increased the mist carryover into the absorber.

- Essentially all of the chloride in the flue gas (35 ppm average) was removed in the venturi section at the anticipated normal operating conditions.

In order to minimize mist carryover during absorber tests, the venturi prewash section was operated at as low a pressure drop and L/G as possible consistant with good humidification. Based on actual operation, these conditions are a pressure drop of 5 to 6 inches of water and an L/G of about 10.

There were three major problem areas identified during the operation of the prewash section (1) low pH of sump liquor (corrosion), (2) disposal of low pH purge water from prewash sump, and (3) mist carryover from the prewash section to the absorber section.

During initial operation, the quantity of makeup water added to the prewash section was that consumed in the process for humidification and absorber product liquor bleedoff, approximately 1.2 gpm. At this flow rate, the pH of the wash liquor was 1.0 or less. The makeup water throughput was increased to 15-30 gallons per minute to increase the pH of the wash water and to reduce its corrosion potential. This raised the pH of the wash water to approximately 2.5, but corrosion continued.

An inspection of the gas pretreatment section was made after 2000 hours of operation. The entire pretreatment section, constructed of Type 316L stainless steel, was badly damaged by corrosion. The rods across the throat of the venturi were pitted badly, especially on the ends, and several needed replacing. The liquor sump walls were corroded with the most severe attack above the normal gas-liquor interface. In this area, pits 40 to 60 mils deep were common. The gas duct from the sump to the absorber and the sample probes inside the duct (316 S.S.) were also severely corroded.

The gas prewash section was operated "open loop" to minimize corrosion of the equipment. The problem of disposing and/or utilizing low pH water will be common to most SO_2 removal processes that require a prewash. It is recognized that in a commercial operation, this loop would have to be closed to meet environmental regulations. Attempts to close the loop around the prewash section will be studied in future operations.

Mist carryover from the venturi section to the absorber dilutes the absorber product liquor and transports dissolved and undissolved solids into the absorber section. Both of these problems are discussed in more detail in the absorber section of this paper.

Currently, the prewash section is being redesigned to resolve the corrosion and mist carryover problems. To protect against corrosion, the sump and exit gas ducts will be constructed of FRP; the venturi throat will probably be lined with neoprene. Several types of corrosion-resistant materials will be tested for use as rods in the venturi. The new prewash section will include a mist eliminator (probably a chevron in the horizontal position) to reduce the amount of carryover to the absorber.

SO_2 Absorber. The absorber shell consists of 32-inch by 32-inch by 4-foot sections. At normal operating conditions, the gas velocity in the tower is approximately 7 feet per second. Two types of absorption elements, marble beds and valve trays, have been tested.

A two-pass chevron mist eliminator is located in the vertical position above the top absorption stage.

Two series of tests were run during the past year. During the first test period, the absorber consisted of one valve tray followed by two marble beds, Figure 3. Tests were made to determine the highest liquor concentration that could be obtained using this configuration while limiting the outlet SO_2 concentration to ≤ 250 ppm and the ammonia concentration to ≤ 50 ppm. Product liquors with high concentrations require less energy for regeneration and smaller regeneration equipment.

The maximum product liquor concentration obtained using this configuration was a C_A (mols of active ammonia present as sulfite and bisulfite per 100 mols of total water) value of 14. Factors limiting the C_A in the initial series were (1) the diluting effect of the mist carryover from the gas pretreatment section and (2) the SO_2 and NH_3 vapor pressure over the liquor on the top stage. An increase in the concentration of the product increases the liquor concentrations throughout the tower. An additional absorption stage was required to reduce the ammonia and SO_2 vapor pressure over the liquor on the top stage to meet the arbitrarily set limits.

The second series of texts was made with the fourth stage added to the absorber. Figure 4 shows the absorber arrangement after addition of the fourth absorber stage. The two marble-bed absorption elements were replaced with valve trays during the modification because of occasional excessive stage-to-stage weepage which upset the liquor concentrations throughout the absorption tower. Experience showed that this problem does not occur with the valve tray when the gas flow rate remains relatively constant although weepage from the valve trays is a problem when the gas flow varies.

Tests using this absorber arrangement indicated that product liquor could be produced that had C_A's of 20 and above. Table 1 shows data from the absorber operation while producing liquor with a C_A of 21. No absorber operational problems were encountered during operation at the high concentration.

After determining that high liquor concentrations could be produced in the modified absorber, it was operated to produce liquor with C_A's of 12 to 15 for use in the regeneration section. Table 2 shows typical data from this operation. Solutions with concentrations in this range are acceptable for regeneration in the ammonium bisulfate process and are much easier to achieve within the limits of SO_2 and ammonia loss and plume emission than are the more concentrated solutions.

The most apparent problem in the absorption step is that of fume formation, Figure 5. From results previously reported by TVA on

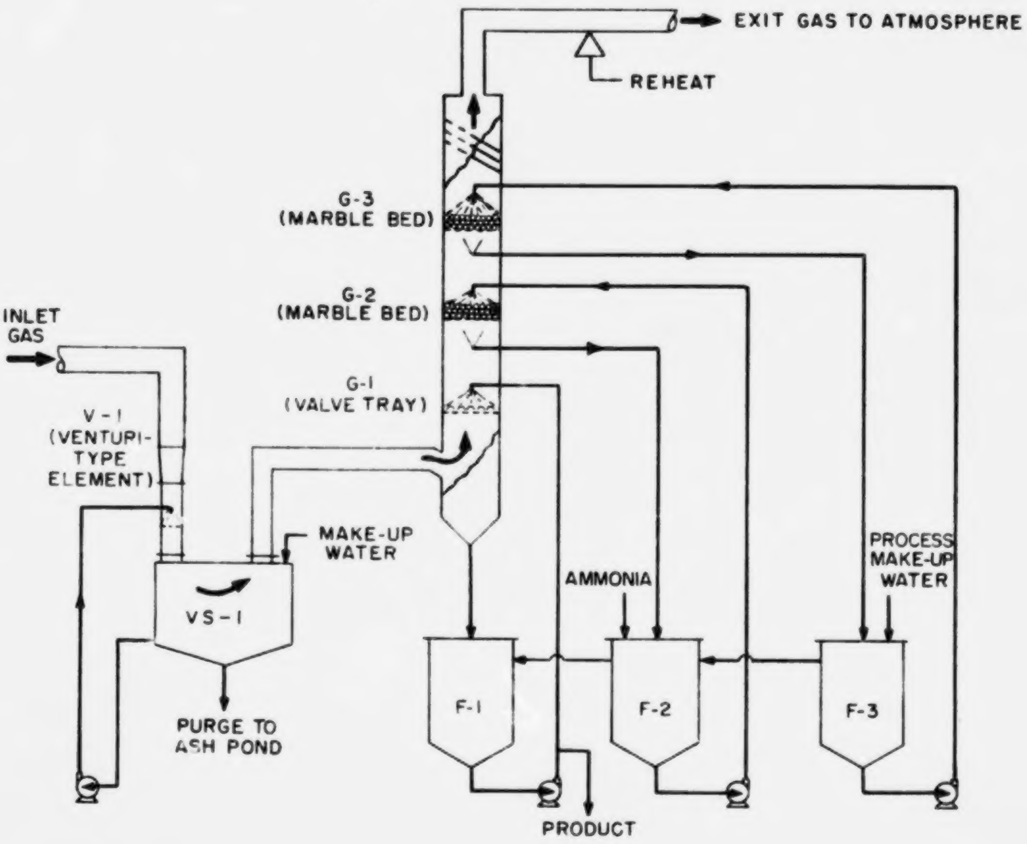
EXIT GAS TO ATMOSPHERE
REHEAT
G-3
(MARBLE BED)
G-2
(MARBLE BED)
G-1
(VALVE TRAY)
INLET
GAS
V-1
(VENTURI-
TYPE
ELEMENT)
MAKE-UP
WATER
VS-1
PURGE TO
ASH POND
AMMONIA
PROCESS
MAKE-UP
WATER
F-1
F-2
F-3
PRODUCT

Figure 3. Three-stage absorption.

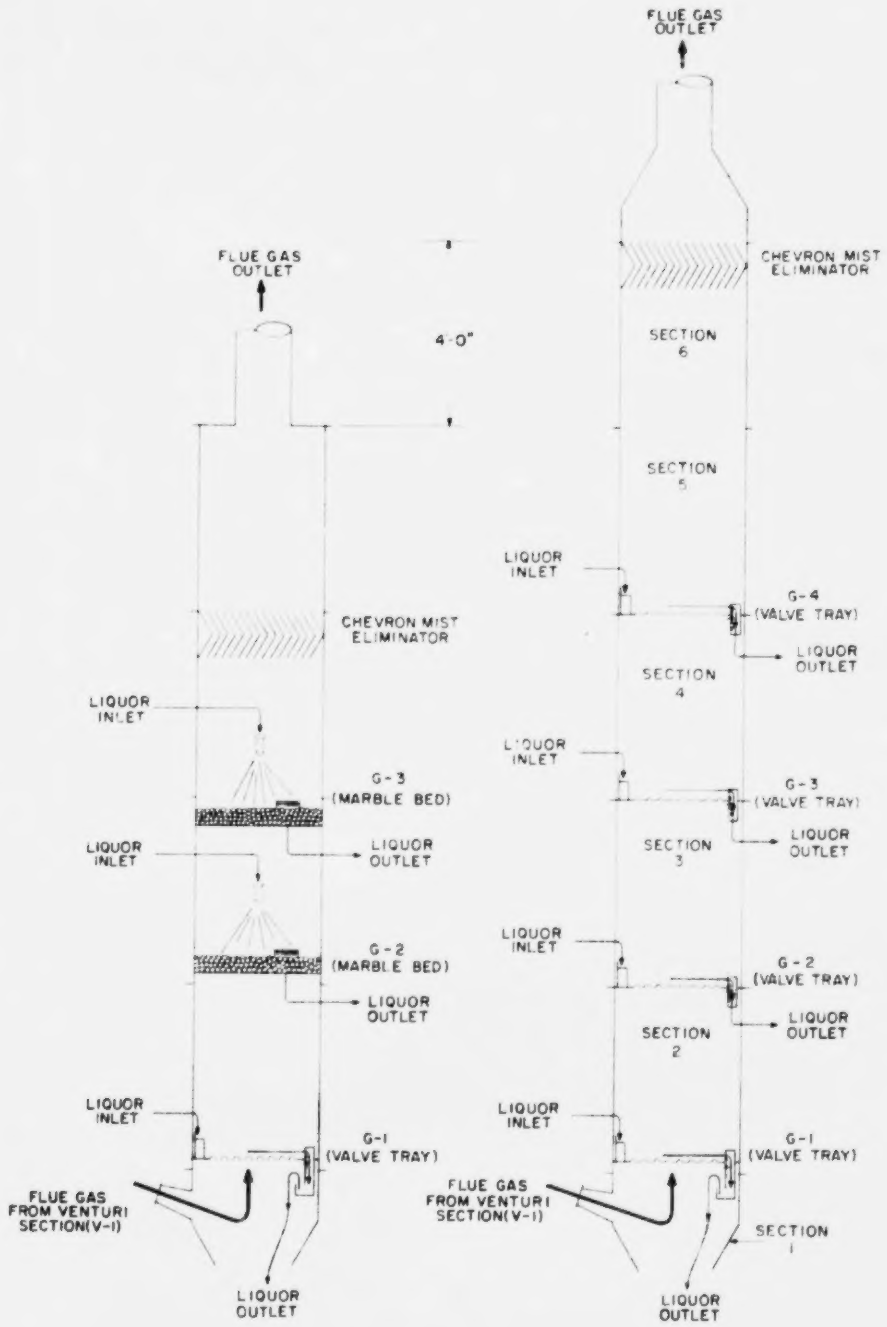
FLUE GAS OUTLET
4'-0"
CHEVRON MIST ELIMINATOR
LIQUOR INLET
G-3 (MARBLE BED)
LIQUOR OUTLET
LIQUOR INLET
G-2 (MARBLE BED)
LIQUOR OUTLET
LIQUOR INLET
G-1 (VALVE TRAY)
FLUE GAS FROM VENTURI SECTION(V-1)
LIQUOR OUTLET
FLUE GAS OUTLET
CHEVRON MIST ELIMINATOR
SECTION 6
SECTION 5
LIQUOR INLET
G-4 (VALVE TRAY)
LIQUOR OUTLET
SECTION 4
LIQUOR INLET
G-3 (VALVE TRAY)
LIQUOR OUTLET
SECTION 3
LIQUOR INLET
G-2 (VALVE TRAY)
LIQUOR OUTLET
SECTION 2
LIQUOR INLET
G-1 (VALVE TRAY)
FLUE GAS FROM VENTURI SECTION(V-1)
SECTION 1
LIQUOR OUTLET

Figure 4. Three- and four-stage absorber.

TABLE 1. TYPICAL ABSORBER LOOP TEST—AMMONIUM BISULFATE PILOT PLANT

Test Conditions

Gas to absorber	
Flow rate, scfm at 32°F	2350
Temperature, °F	295
SO_2, ppm	2800
Gas leaving venturi	
Temperature, °F	120
SO_2, ppm	2720
Gas leaving first stage	
Temperature, °F	123
SO_2, ppm	1160
Gas leaving second stage	
Temperature, °F	124
SO_2, ppm	430
Gas leaving third stage	
Temperature, °F	115
SO_2, ppm	510
Gas leaving fourth stage	
Temperature, °F	114
SO_2, ppm	390
SO_2 removal, %	84
Fresh water feed to absorber, gpm	0.2
Ammonia feed to absorber, lb/hr	22.5
Liquor flow from first stage to second stage, gpm	1.6
Liquor to first stage (product)	
C_A	21.1
S/C_A	0.73
pH	6.2
Specific gravity	1.286
Liquor to second stage	
C_A	21.5
S/C_A	0.67
pH	6.3
Specific gravity	1.282
Liquor to third stage	
C_A	6.6
S/C_A	0.78
pH	5.9
Specific gravity	1.138
Liquor to fourth stage	
C_A	2.5
S/C_A	0.86
pH	5.7
Specific gravity	1.086

TABLE 2. TYPICAL ABSORBER LOOP TEST—AMMONIUM BISULFATE PILOT PLANT

Test Conditions	
Gas to absorber	
Flow rate, scfm at 32°F	2350
Temperature, °F	305
SO_2, ppm	2680
Gas leaving venturi	
Temperature, °F	123
SO_2, ppm	2520
Gas leaving first stage	
Temperature, °F	121
SO_2, ppm	1240
Gas leaving second stage	
Temperature, °F	122
SO_2, ppm	330
Gas leaving third stage	
Temperature, °F	116
SO_2, ppm	320
Gas leaving fourth stage	
Temperature, °F	115
SO_2, ppm	230
NH_3, ppm	10
SO_2 removal, %	91
Fresh water feed to absorber, gpm	0.3
Ammonia feed to absorber, lb/hr	21.5
Liquid flow from first stage to second stage, gpm	0.74
Liquor to first stage (product)	
C_A	14.7
S/C_A	0.80
pH	5.9
Specific gravity	1.236
Liquor to second stage	
C_A	15.3
S/C_A	0.66
pH	6.4
Specific gravity	1.220
Liquor to third stage	
C_A	4.0
S/C_A	0.84
pH	5.9
Specific gravity	1.093
Liquor to fourth stage	
C_A	1.6
S/C_A	0.94
pH	5.6
Specific gravity	1.042

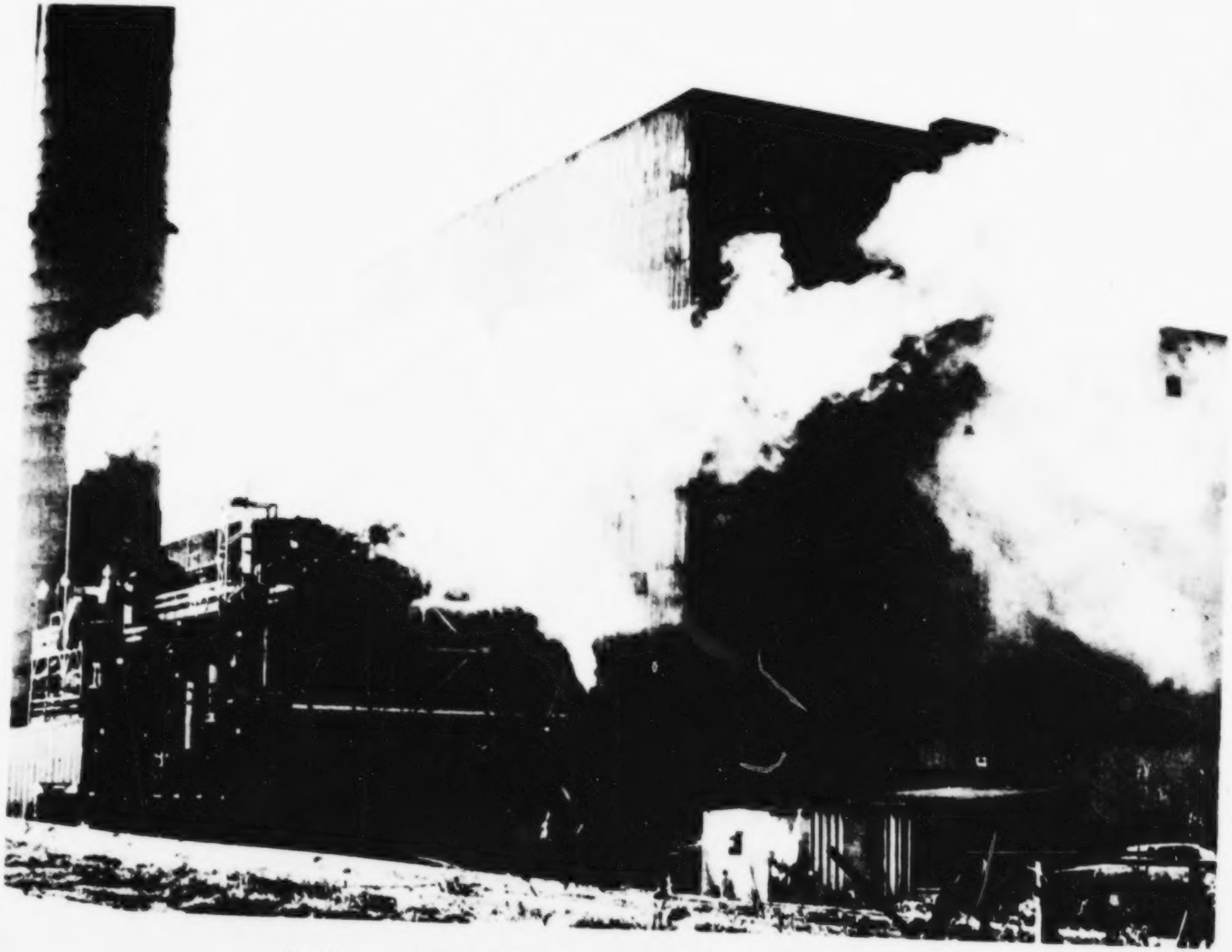

Figure 5. Unacceptable plume during routine operation; product from absorber: $C_A = 10.0$. $S/C_A = 0.8$; no reheat.

the use of a single-stage marble-bed absorber, it was concluded that an acceptable plume (defined as < 5% opacity for this pilot plant) could be obtained when:

- A water wash is used ahead of the absorption stage.
- The absorber and all ducts are insulated.
- Reheat is applied as required to dissipate the steam plume.

Additional tests were run using a single-stage valve tray absorber, Figure 6, to obtain data on the plume emitted from an uninsulated absorber as compared with an insulated absorber. The absorption stage was sandwiched between two water-wash stages. Either or both of the water stages were turned off to determine the effect on plume opacity. The C_A values of the absorption liquor tested were 2, 7, and 12. The S/C_A ratio (mols of SO_2 present as sulfite and bisulfite per mol of active ammonia present as sulfite and bisulfite) was controlled near 0.8. The exit gas was reheated to 140° and 175°F in each test.

The water wash from the bottom decreased the plume opacity in all cases. The water wash was not used in Figure 7 and the plume opacity was 5 to 10%. The water wash was activated and the opacity decreased to 0%, Figure 8. The same amount of reheat (200°F) was applied in both cases to eliminate the steam plume. The water wash from above lowered the opacity only at a C_A of 12. The combination of a water wash on the bottom tray and reheat resulted in an opacity of 5% or less for all three levels of C_A's, Figures 9, 10, and 11.

The plume was also observed during multistage absorber operation. The insulated absorber shown in Figure 3 contained three absorption stages (one valve tray and 2 marble beds) preceded by a prewash section.

A steam and particulate plume was emitted from the absorber in these multistage absorber tests. In most cases, a reheated exit gas temperature of 10° to 20°F above the calculated value at which the steam plume should dissipate was required to reduce the plume to less than or equal to 5% opacity, Figure 12. A previous test series, reported at the Flue Gas Desulfurization Symposium in New Orleans last year, indicated that a single-stage absorber could be operated with an acceptable plume while reheating to or just above the calculated temperatures. The only operational changes made in comparison to the previous series were three stages of absorption versus one and higher liquor concentration on all stages. Mist carryover from the more concentrated liquor on the top stage probably accounts for the increase in reheat temperature required to maintain the same opacity. During reheat, the mist is evaporated, thus increasing the vapor pressure of SO_2 and NH_3 in the exit gases. A plume then results from the gas phase reaction of SO_2 and ammonia in the presence of water in the gas duct and/or in the atmosphere.

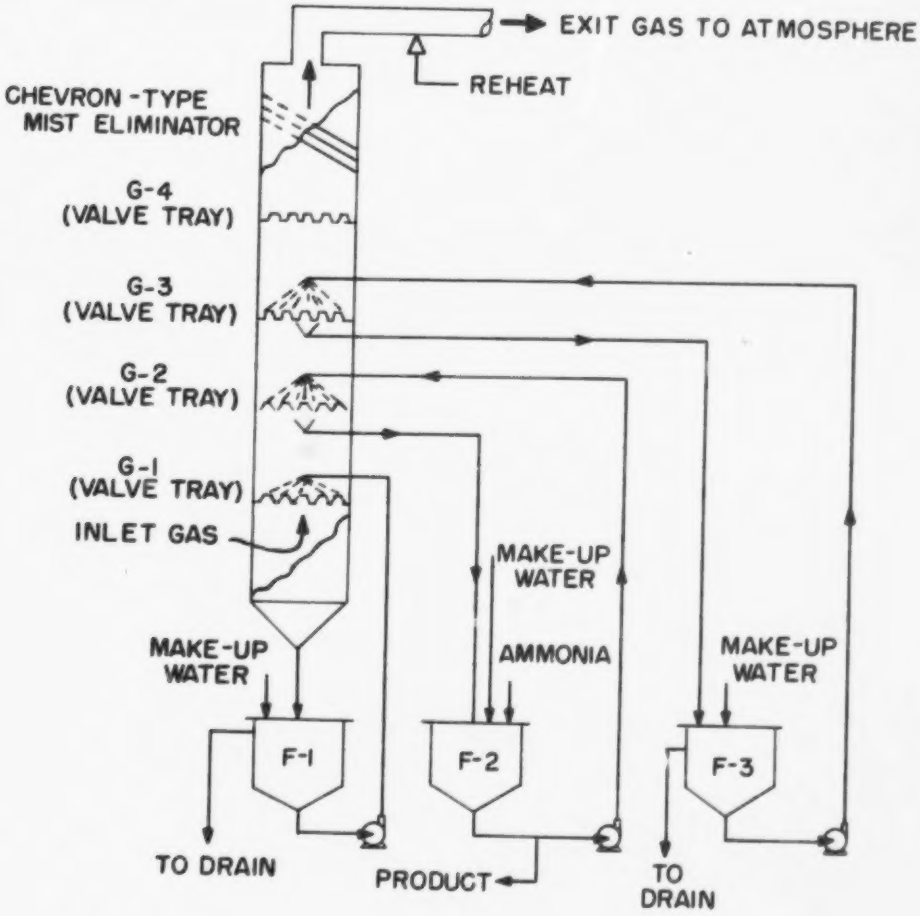
EXIT GAS TO ATMOSPHERE
REHEAT
CHEVRON -TYPE MIST ELIMINATOR
G-4 (VALVE TRAY)
G-3 (VALVE TRAY)
G-2 (VALVE TRAY)
G-1 (VALVE TRAY)
INLET GAS
MAKE-UP WATER
AMMONIA
MAKE-UP WATER
MAKE-UP WATER
F-1
F-2
F-3
TO DRAIN
PRODUCT
TO DRAIN

Figure 6. Single-stage valve-tray absorber.

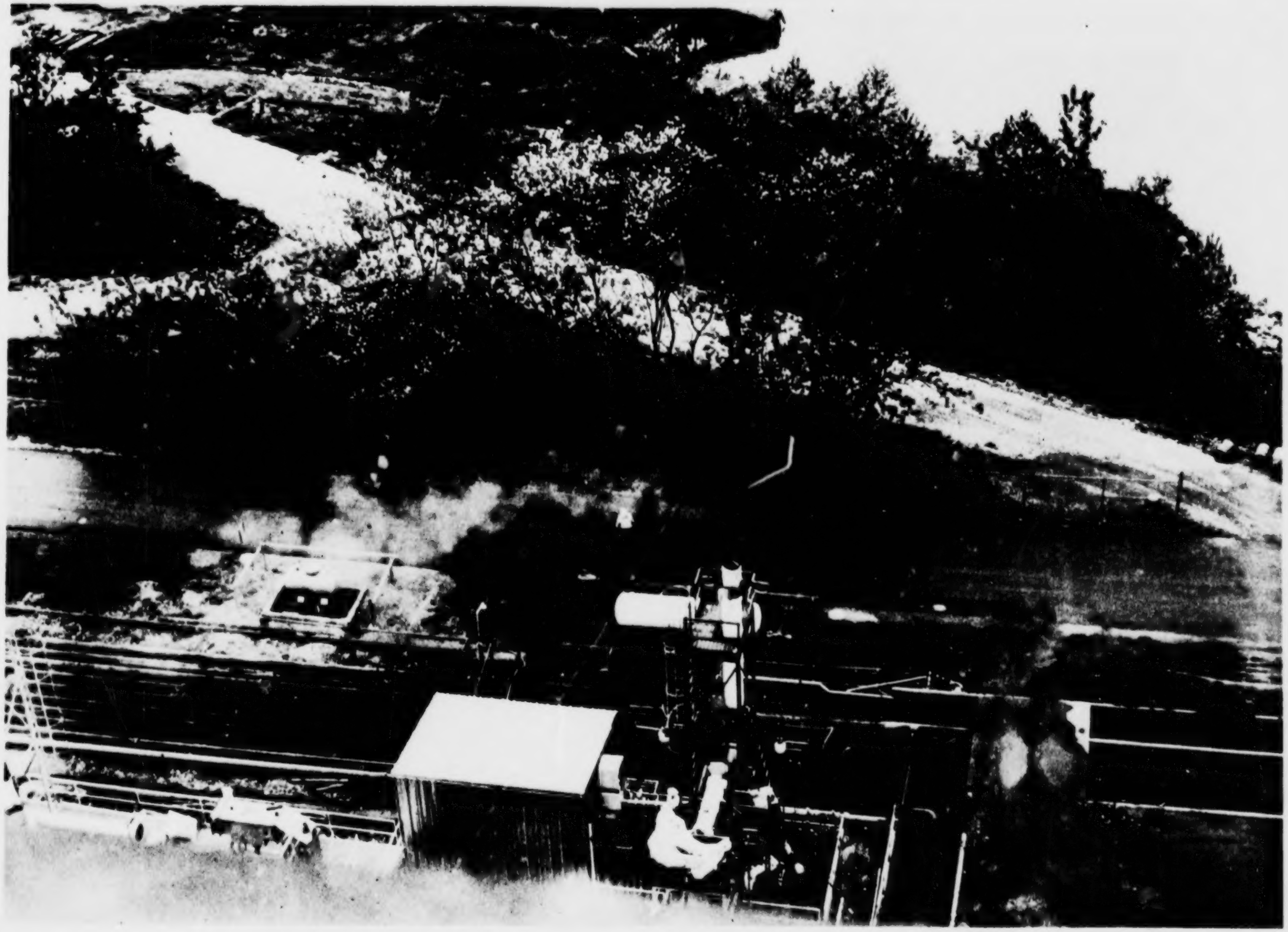

Figure 7. Operation with no water wash ahead of first absorber stage; 200°F reheat; 5 to 10% opacity.

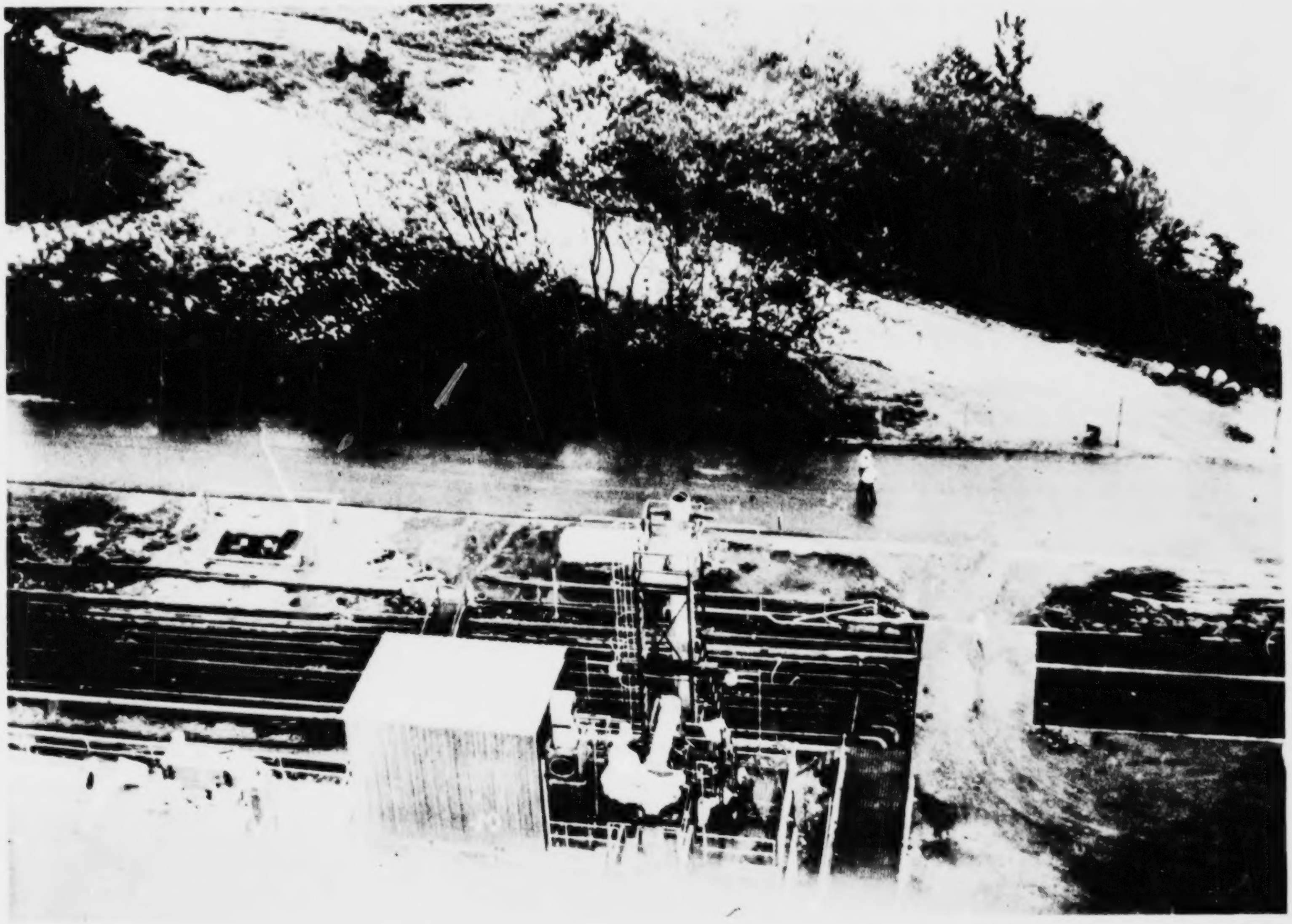

Figure 8. Operation with water wash ahead of first absorber stage; 200°F reheat; 0% opacity.

Figure 9. Plume from operation with product solution having $C_A = 2$; one absorber stage sandwiched between two water wash stages; no insulation; 142°F reheat; 0% opacity.

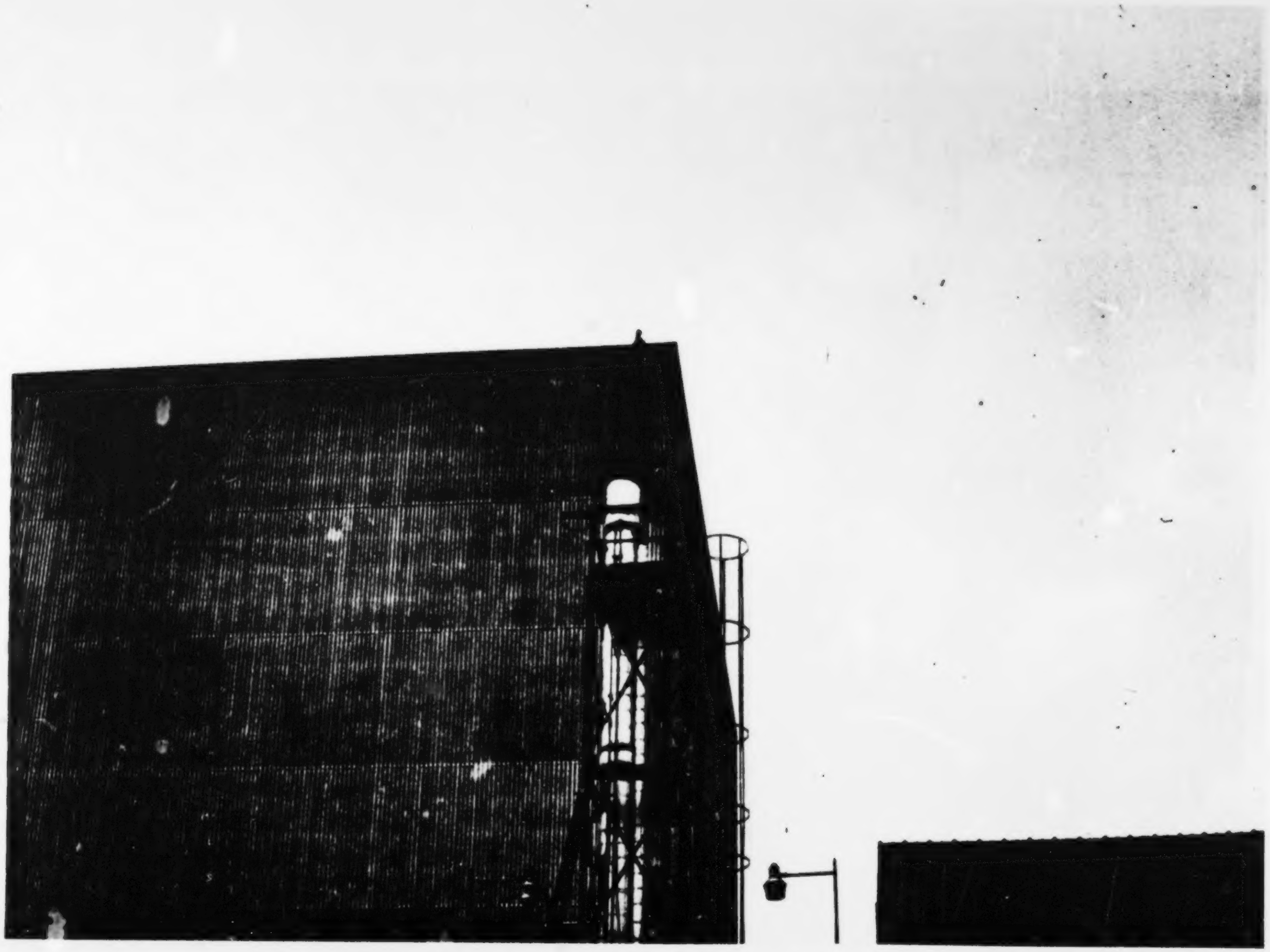

Figure 10. Plume from operation with product solution having $C_A = 7$; one absorber stage sandwiched between two water wash stages; no insulation: 141°F reheat; 0% opacity.

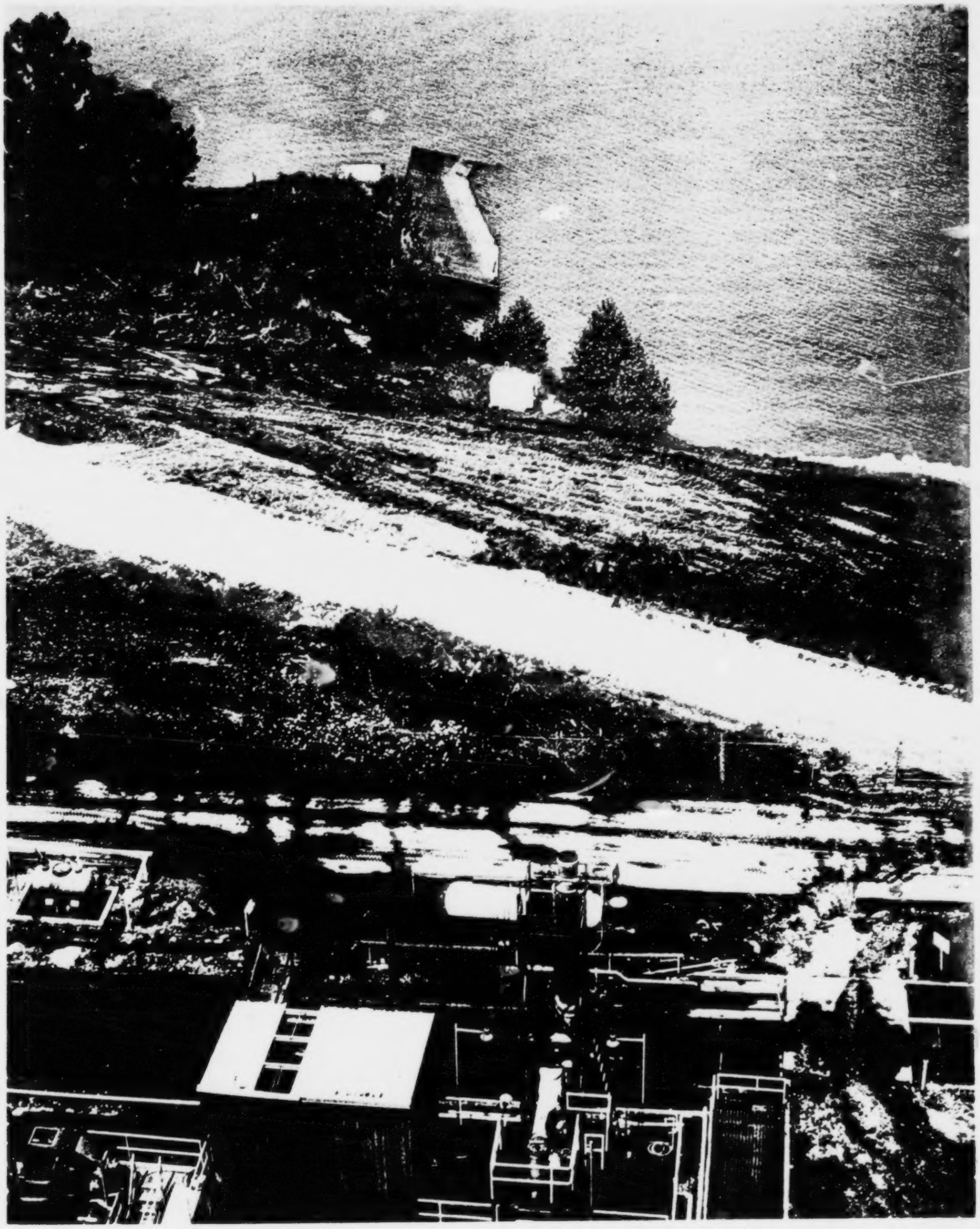

Figure 11. Plume from operation with product solution having $C_A = 12$; one absorber stage sandwiched between two water wash stages; no insulation; 175°F reheat; 0% opacity.

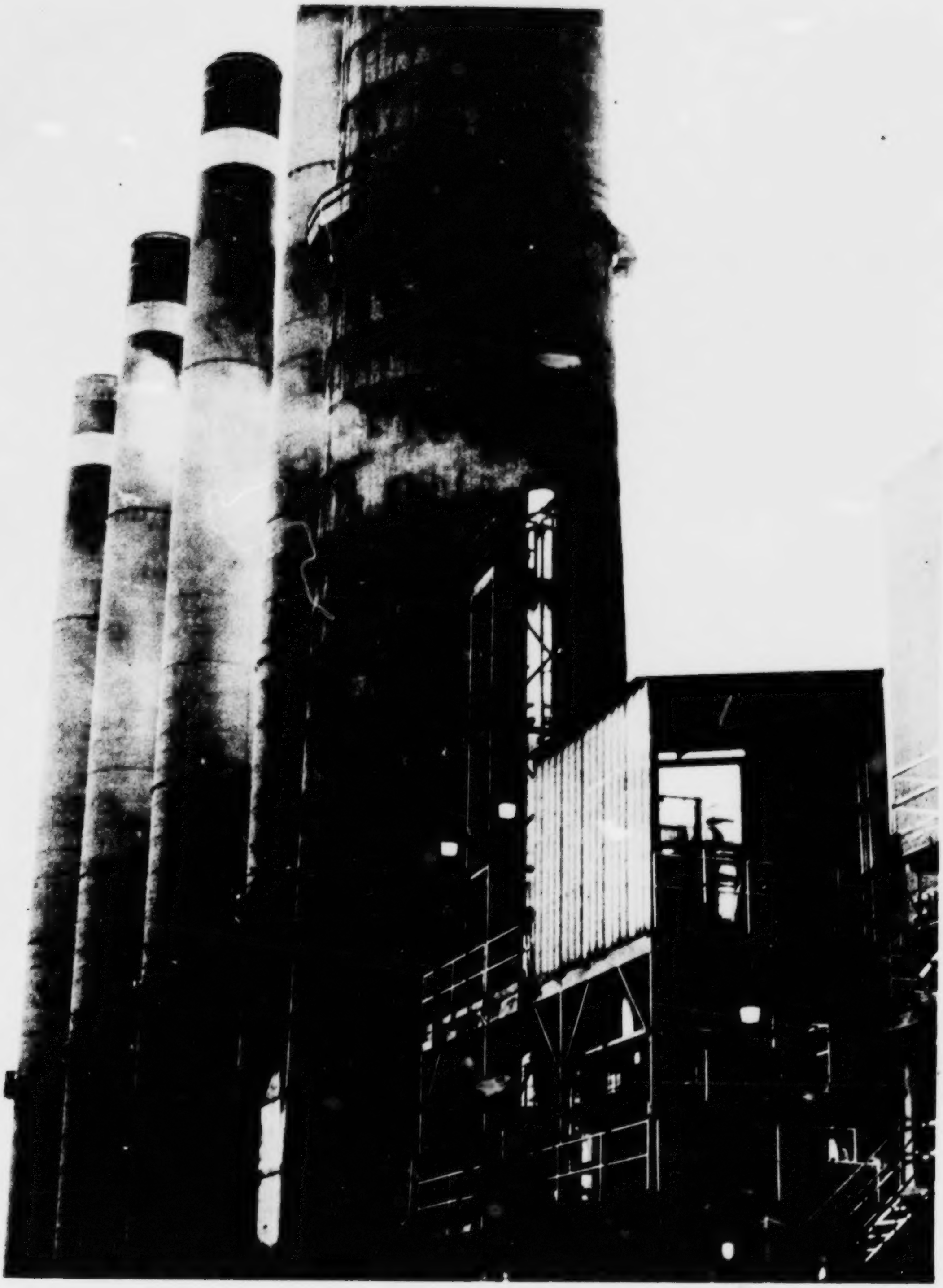

Figure 12. Plume from operation with product having $C_A = 14$; three absorber stages preceded by a water wash stage; 180°F reheat; 5% opacity.

When the fourth absorption stage was added to the tower, the insulation was removed and not replaced. As in the 3-stage insulated absorber operation, the plume from the uninsulated 4-stage absorber was controlled at 5% opacity in most cases by reheating the exit gas 10° to 20°F above the temperature required to dissipate the steam plume, Figure 13.

The use of the prewash, the reheat, and dilute solutions at the top of the tower are considered necessary in controlling the plume from the absorber. The value of insulating the absorber has not been fully evaluated by TVA and no recommendations can be made at this time.

In all cases, the ambient weather conditions have an overriding effect on plume emission. On cold wet days, the plume cannot be reheated to a high enough temperature to eliminate the plume. On warm days with high humidities, the plume reforms outside the absorber 10 to 20 feet downwind of the stack.

In two sampling and analysis series conducted about two months apart, EPA measured the levels of ammonia and SO_2 in the exit gas as 1.48 ± 4.17 ppm and 234 ± 88 ppm, respectively. Particulate mass emissions and particulate size distribution of the effluent particulate were also determined by EPA. The measured effluent particulate emission concentration was 0.057 ± 0.015 gr/dscf and 0.127 ± 0.015 gr/dscf. Calculations indicate that the measured particulate concentration in the exit gas could not totally be accounted for via the gas phase reaction between NH_3 and SO_2 but was primarily due to mist carryover from the absorber. Size distribution analysis indicated that 88.1% ± 2.6 of the particulate was finer than about 2 microns and that 61.7 ± 9% of the emitted particulate was finer than about 0.8 micron. Analysis of the emitted particulate by X-ray defraction technique and wet chemical methods indicated that the particulate was pure ammonium sulfate. As stated earlier, this particulate loading is believed to be the result of carryover.

The precipitation of solids in the absorption section may present another major problem. A yellow solid, tentatively identified petrographically as a homogeneous iron-ammonia-sulfur compound was present in all of the absorber liquors. Fly ash is the probable source of iron in the solid. Although most of the fly ash is removed in the prewash section, some passes through the venturi and is removed in the absorber. The mist carryover from the prewash section also contains dissolved iron along with other metals.

A small quantity of the solids in the product liquor may be sufficient to adversely affect the production of crystalline ammonium sulfate in the regeneration section. Also the solids contain iron which may catalize the decomposition of ammonia during thermal decomposition of ammonium sulfate. Attempts to remove the solids by filtration were unsuccessful because the precipitated solids and fly ash form a gelatinous, thixotropic material (Figure 14) that blinded the filter media. The material is removed from the product liquor in the pilot plant by settling in the product storage tanks and then decanting the clear supernatant liquor for use in the regeneration section. This method of solids separation is acceptable for the pilot-plant operation but may prove impractical for a commercial operation.

Figure 13. Plume from operation with product liquor having C_A = 14% four absorber stages preceded by a water wash stage; 155°F reheat; 5% opacity.

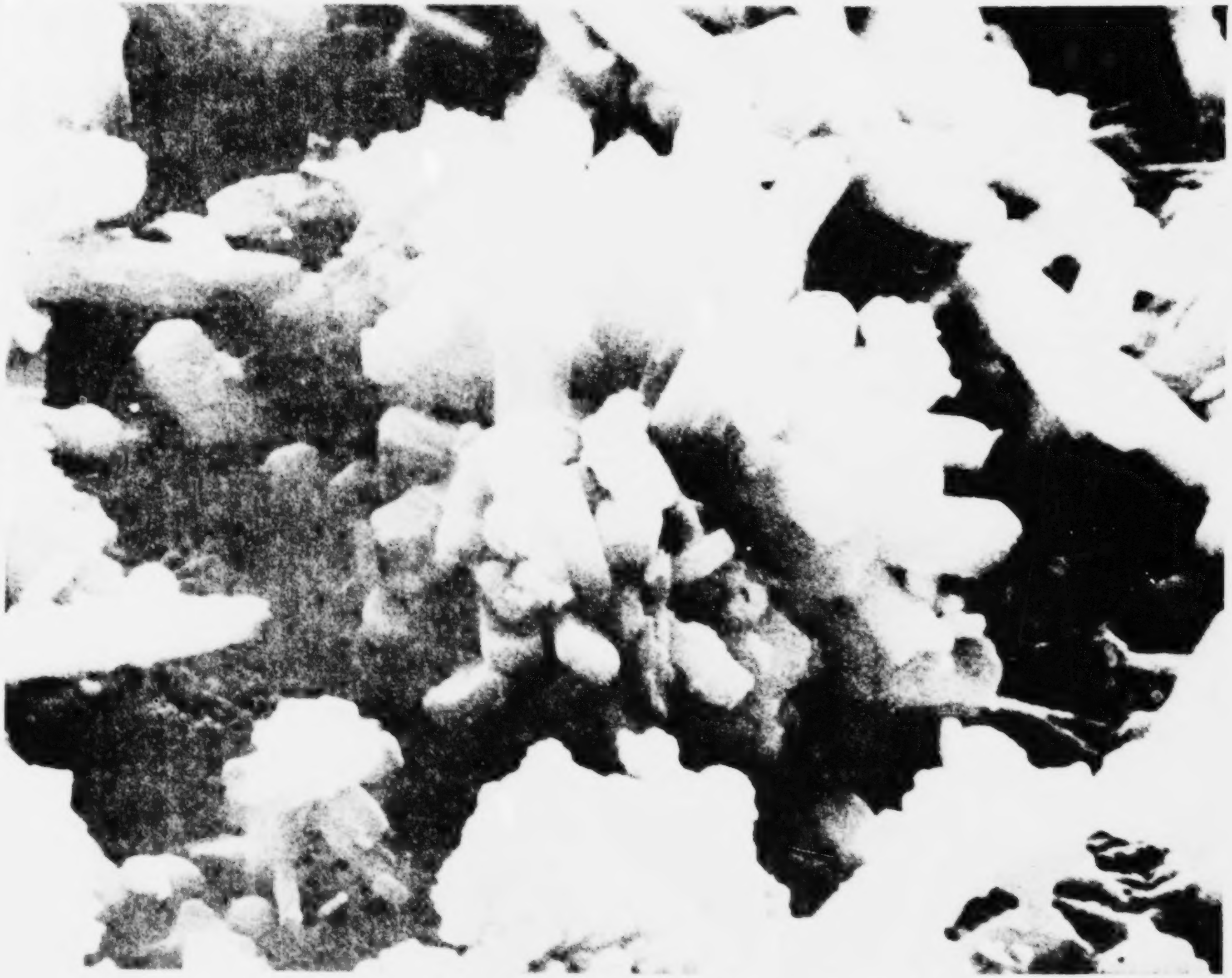

Figure 14. Photomicrograph of solids precipitated is the absorber loop mixed with fly ash.

Oxidation of sulfite to sulfate occurred in the absorption section. In the range of liquor concentrations tested, the oxidation ranged from 10 to 15% of the absorbed SO_2. An average value of 13% was obtained over an extended operating period using the 4-stage absorber. This oxidation byproduct would have to be purged from a closed-loop system and probably sold as a fertilizer.

An equipment inspection of the absorption tower was made to locate the areas in which corrosion is a problem.

The absorber shell, shown in Figure 15, is a combination of six 4-foot sections salvaged from various absorbers. Data pertinent to each section are:

Section	Description	Exposure, hr	Material of construction, Type stainless steel
1	Transition piece for gas inlet and liquor outlet	14,000	316
2	Section between first and second absorption stages	10,000	304
3	Section between second and third absorption stages	4,000	304
4	Section between third and fourth absorption stages	4,000	304
5	Section between fourth stage and demister	14,000	316
6	Demister housing	10,000	304

The first section, which has been in service 14,000 hours, had only a few small pits. The second and sixth sections, exposed for 10,000 hours, were severely pitted. The third and fourth sections, exposed for 4000 hours, contained very few pits. The fifth section was used for about 13,000 hours as an exhaust duct after the demister and for about 1000 hours as a housing for an absorbing element. The walls of this section were severely pitted; most of the pitting occurred in the location above the demister.

The tower contains four Type 316 stainless steel absorption trays (valve trays) spaced 4 feet apart. The bottom tray (G-1) was used for about 3100 hours, and the three upper trays (G-2, 3, and 4) were used about 700 hours. The bottom side of G-1 was pitted, but the top side showed little corrosion. The support angles located below the tray (Type 316 or 304) were severely pitted. Some of the internal piping

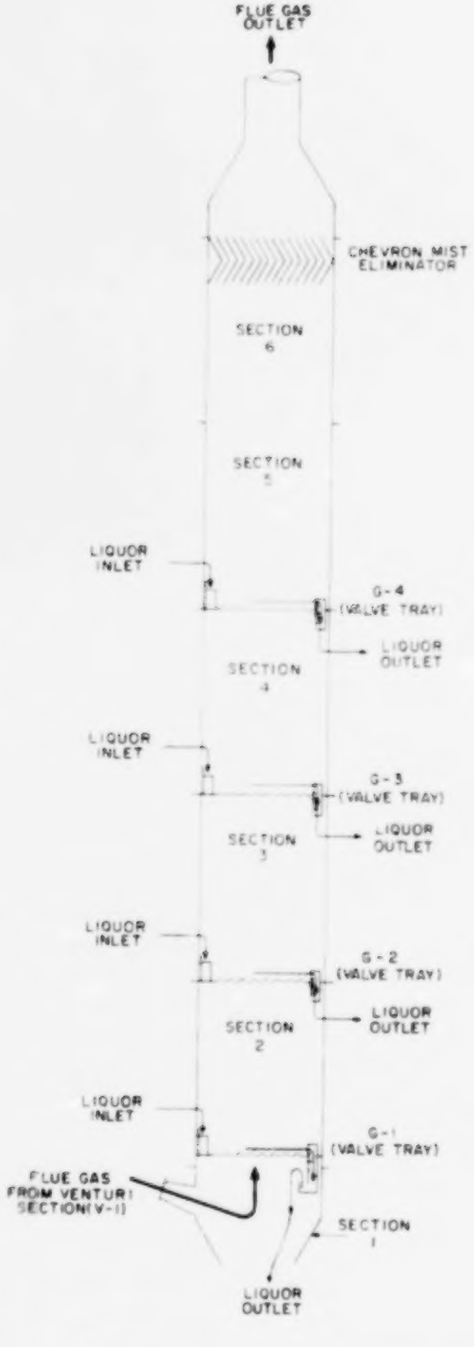
FLUE GAS OUTLET
CHEVRON MIST ELIMINATOR
SECTION 6
SECTION 5
LIQUOR INLET
G-4 (VALVE TRAY)
LIQUOR OUTLET
SECTION 4
LIQUOR INLET
G-3 (VALVE TRAY)
LIQUOR OUTLET
SECTION 3
LIQUOR INLET
G-2 (VALVE TRAY)
LIQUOR OUTLET
SECTION 2
LIQUOR INLET
G-1 (VALVE TRAY)
FLUE GAS FROM VENTURI SECTION(V-1)
SECTION 1
LIQUOR OUTLET

Figure 15. Absorber shell.

(probably Type 304) to the tray was severely pitted while other sections (Type 316) were only slightly affected. The temperature of the liquor normally in contact with the bottom tray was 125°F (52°C) with an average pH of 5.8 and a C_A value of 8–20.

The bottom tray was used for about 1200 hours of its total exposure time, as a water wash stage and for humidification of the inlet flue gas. During this time, the operating conditions were similar to the operating conditions of the venturi. Most of the corrosion probably occurred during this time.

The second, third, and fourth trays (G–2, 3, and 4), supports, and internal piping showed no signs of corrosion after the 700 hours of operation. The temperature of the absorbing liquor on these stages was approximately 120°F; the pH value ranged from 5.4 to 7.0.

The chevron mist eliminator is located in the uppermost 4–foot section of the absorber. This section of the absorber has been in service about 10,000 hours and was corroded severely. Severe pitting, 30 mils deep had occurred where drainage from the mist eliminator flowed down the walls. The top and bottom of the mist eliminator blades were badly pitted.

The transition piece (Type 316L stainless steel) that joins the top of the absorber to the 14–inch–diameter flue gas exit duct has been in service for about 700 hours with no apparent corrosion.

Conclusions drawn from the equipment inspection are:

- Type 316 stainless steel is not suitable for use in the prewash (venturi) section.
- Type 316 stainless steel is suitable for service in the absorber shell and in the internal piping.
- Use of Type 304 stainless steel, which pitted badly in the absorber shell and piping when exposed for 10,000 hours, is marginal.
- The demist section is subject to severe corrosion, and use of both Types 304 and 316 stainless steel in this area is marginal.

Regeneration Section

A flowsheet of the regeneration section of the pilot plant is shown in Figure 16. The absorber product liquor is fed to an acidulator. Here the liquor is mixed with an acid ion to chemically release the SO_2. A portion of the released SO_2 is evolved in the acidulator. In past operation, the acid ion was supplied by plant grade sulfuric acid. In an intergrated ABS system, the acid ion will be supplied by ammonium bisulfate generated by thermal decomposition of ammonium sulfate.

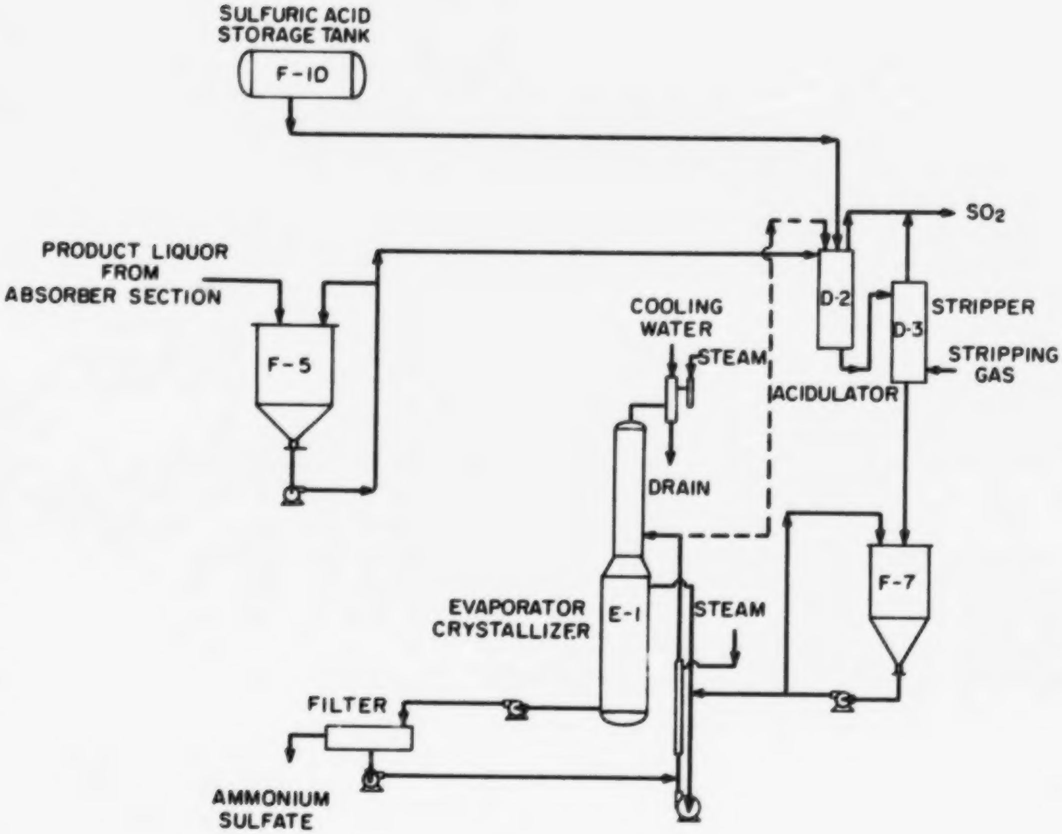
SULFURIC ACID
STORAGE TANK
F-10
SO2
PRODUCT LIQUOR
FROM
ABSORBER SECTION
F-5
COOLING
WATER
STEAM
D-2
D-3
STRIPPER
STRIPPING
GAS
ACIDULATOR
DRAIN
F-7
EVAPORATOR
CRYSTALLIZER
E-1
STEAM
FILTER
AMMONIUM
SULFATE

Figure 16. Regeneration section.

The liquor from the acidulator overflows into a stripper where the remaining SO_2 is stripped from the liquor with a countercurrent flow of air.

The stripped liquor (ammonium sulfate solution) is metered into the evaporator-crystallizer where water is evaporated to produce a slurry of ammonium sulfate crystals. The crystals are separated from the mother liquor in a continuous belt filter and dried. The crystals will be fed to the ammonium sulfate decomposer when it is available.

A discussion of the individual steps follows.

Acidulation and Stripping. The acidulation and stripping vessels are shown in Figure 17. The acidulator is constructed from a 6-foot section of a 12-inch stainless steel pipe and is coated internally with DuPont's TFE Teflon for corrosion protection. A cone mixer, located at the top of the acidulator, is used for mixing the absorber product liquor with sulfuric acid. The acidulator is mounted so that the point of gravity overflow to the stripper can be raised or lowered to vary the retention time of the material in the acidulator.

The stripping vessel was constructed of a 6-foot length of 12-inch stainless steel pipe and the inside was coated with Teflon. The stripper contains a 4-foot section of packing (polypropylene Pall rings). Acidulated liquor enters the top of the vessel and flows countercurrent to a stream of stripping gas (air) entering the vessel near the bottom. The SO_2 stripped from the liquor joins the SO_2 released in the acidulator and is routed back to the power plant ductwork. The stripped liquor (ammonium sulfate solution) is then fed to the evaporator crystallizer.

Typical data from a series of acidulation and stripping operations are shown in Table 3. In these tests, liquor from the absorption section having a C_A value of 14.7 was metered to the acidulator. Sulfuric acid (93%) was also metered to the acidulator at a rate to give an acid ion to ammonia ion ratio of 1.5. The liquor and acid were at ambient temperature (about 80°F). Stripping gas (air) also at ambient temperature was used to remove the chemically released SO_2 from the solution. The air flow rate was 10 cfm (30 cfm/gal of solution). Under these conditions, 96% of the SO_2 in the ammonium sulfite - bisulfite liquor to the acidulator was removed during the acidulation and stripping operation.

The SO_2 remaining in the acidulated and stripped liquor is released in the evaporation-crystallization step and leaves the process with the steam from this equipment. Because this is a potential pollution problem additional efforts are being made to further decrease the SO_2 remaining in the acidulated and stripped liquor. New designs for both the acidulator and stripper are being considered to improve the SO_2 release from this operation.

The acidulator and stripper were inspected after 1800 hours of operation. The Teflon coating in the acidulator had failed and was

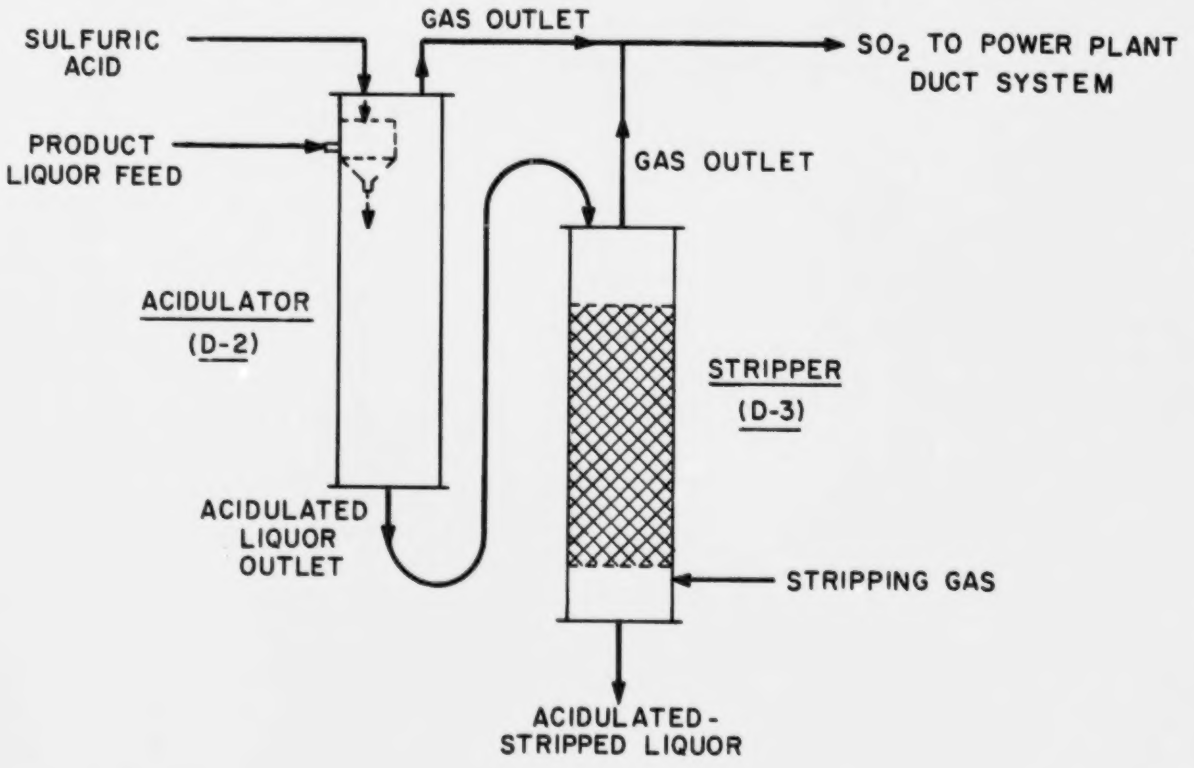
SULFURIC ACID
PRODUCT LIQUOR FEED
GAS OUTLET
SO_2 TO POWER PLANT DUCT SYSTEM
GAS OUTLET
ACIDULATOR
(D-2)
STRIPPER
(D-3)
ACIDULATED LIQUOR OUTLET
STRIPPING GAS
ACIDULATED-STRIPPED LIQUOR

Figure 17. Acidulator-stripper.

TABLE 3. TYPICAL REGENERATION LOOP OPERATION

AMMONIUM BISULFATE PILOT PLANT

Test Conditions

Acidulator	
Liquor feed in	
C_A	14.7
S/C_A	0.81
pH	6.2
Specific gravity	1.244
Flow rate, gpm	0.3
Sulfuric acid	
Flow rate, gpm	0.07
Percent sulfuric acid	93
Stoichiometry[a]	1.5
Liquor flow out	
pH	1.8
Specific gravity	1.244
Percent SO_2 release	90
Stripper	
Stripping gas	
Type gas	Air
Flow rate, cfm at 70°F	10
Liquor flow out	
pH	1.9
Specific gravity	1.240
Percent SO_2 release	59
Overall % SO_2 release	96

---

[a] Stoichiometry is the ratio of acid ion to mols NH_3 as ammonium bisulfite and ammonium sulfite.

peeling from the cone mixer and acidulator walls. The exposed stainless steel bottom of the cone mixer was severely damaged. The bare stainless steel acidulator walls were coated with a rust-colored deposit.

The stripper was found to be in good condition. No peeling of the Teflon coating was noted and the Pall rings showed no signs of wear.

Evaporator-Crystallizer. The evaporator-crystallizer used to produce ammonium sulfate from the acidulated and stripped liquor is $\cong$30 feet high, 2 feet in diameter at the bottom, and has a rated capacity of 350 pounds of ammonium sulfate crystals per hour. The entire unit is constructed of Type 316L stainless steel.

The crystallizer was received and installed near the end of the fiscal year and most of the operating time was spent in getting the equipment.to perform according to specifications. Limited tests after operation was established indicated that the evaporator-crystallizer was adequately sized to remove water from the liquor at the highest flow rate anticipated during the test program. Crystals of ammonium sulfate produced in the crystallizer were sent to a belt filter.

Ammonium sulfate removal was accomplished by use of a belt filter and a product dryer which removed the approximately 150 pounds per hour of ammonium sulfate crystals produced in the crystallizer. The belt filter was borrowed from another pilot plant and proved to be greatly oversized for the ABS study. The belt has an effective filtration area of 10 square feet and was operated at its lowest operating speed of about 2 feet per minute. Intermittent operation was required even at the lowest belt speed in order to build a cake thick enough to maintain a vacuum in the system. Hinderance from ferrous ammonium sulfite, the subject of earlier concern, did not materialize and satisfactory filtration rates were obtained.

The crystals were dewatered from about 80% to about 5% water on the belt and were then fed to a propane gas-fired dryer (1 ft dia by 12 ft long). Product from the dryer contained less than 1% water and was free flowing.

Figure 18 is a photograph of a typical group of crystals. Approximately 70% of the crystals were retained on a 35-mesh screen.

Ammonium Sulfate Decomposer. The ammonium sulfate decomposer will be used to decompose the sulfate crystals to ammonia and ammonium bisulfate. The ammonia will be returned to the absorption section and the ammonium bisulfate to the acidulator.

The preliminary project plans for a completed ABS process included a thermal decomposer to be supplied by an outside company. However, the piloting and scaleup of that decomposer which uses direct combustion of petroleum products as the heat source has not been completed. The plans have now been modified to include an electrically heated decomposer. A preliminary design for the pilot unit has been completed using the design criteria listed on page 34.

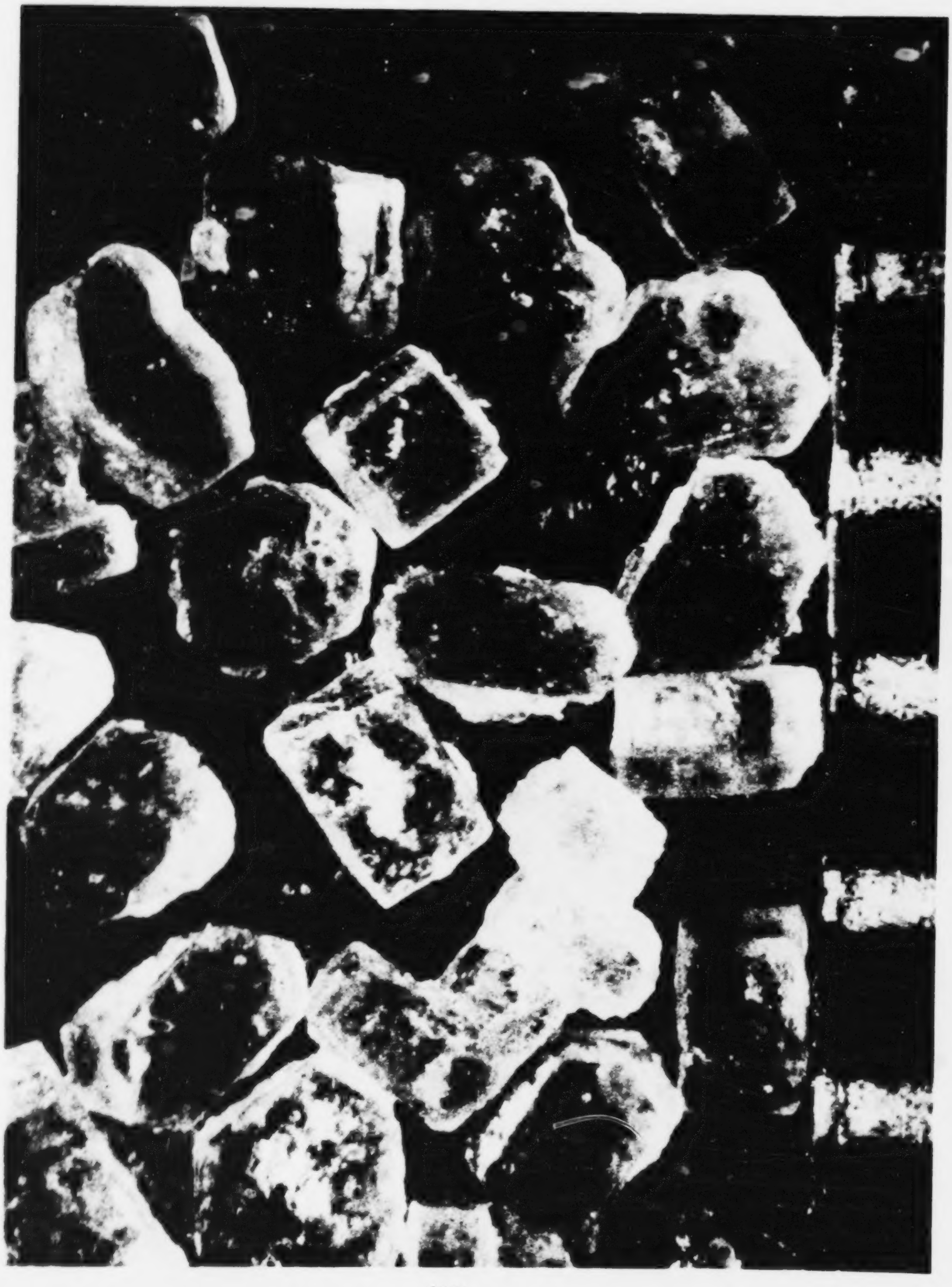

Figure 18. Crystals of ammonium sulfate produced in the ABS process; one scale division = 1 millimeter.

Capacity	≅ 2 MW
Ammonium sulfate feed rate	200–250 lb/hr
Melt temperature	650°–750°F
Melt volume	12–14 cu ft (1500 lb)
Flow rate of melt	2 cu ft/hr (0.25 gpm)
Steam feed rate	40–75 lb/hr at process temp.
Off–gas rate	≅ 3000–5000 cu ft/hr
Net electrical power input to process	45 kW (≅ 350 kWh/ton A/S decomposed)

The design of the decomposer is based primarily on information supplied by Plancor 1865, a United States Government Document[9]. The anticipated delivery date for the unit is fall 1975. Once the decomposer is installed and is on stream, the ABS system will be operated on a cyclic, closed–loop basis to determine long–term operating characteristics of the intergrated process.

Future Studies

Results of past operations have shown that the ammonium bisulfate process is a promising candidate for second generation SO_2 removal systems. Continuing pilot–plant activities will be directed toward long–term operation of an intergrated ABS system and demonstrated performance of 90%+ SO_2 removal. The approach to this objective will include:

- Closing the water balance around the gas prewash section and reducing carryover into the absorber.
- Further reducing the plume emissions from the absorber.
- Improving the acidification and stripping steps to obtain a complete release of SO_2 using ABS melt for acidulation.
- Improving the solids separation from the absorber product liquor.
- Studying ammonium sulfate crystallization (energy required, crystal growth, crystal size, etc.).

CONVERSION OF ENGLISH UNITS TO METRIC EQUIVALENTS

Multiply English Unit	By	To Obtain Metric Equivalent
ft^3/min	0.0283	m^3/min
lb	0.454	kg
°F	$°C = \frac{5}{9} (°F - 32)$	°C
gr/ft^3	2.288	g/m^3
in	2.54	cm
ft	0.3048	m
gal/min	3.785	l/min

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DESCRIPTION AND OPERATION OF THE STONE & WEBSTER/IONICS SO_2 REMOVAL AND RECOVERY PILOT PLANT AT THE WISCONSIN ELECTRIC POWER COMPANY, VALLEY STATION, IN MILWAUKEE

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ABSTRACT

The first phase of the EPA-WEPCO-sponsored program to evaluate the S&W/Ionics closed cycle SO_2 removal system has been completed. The technical feasibility of the process was demonstrated in a 2000 ACFM pilot plant. Average SO_2 removal was 85-95% at exit concentrations of 200-300 ppm SO_2. Oxidation of SO_2 in the absorber varied from 7-25% with a maximum error of measurement of 7%. Other pilot plant results and technical considerations in the design of a prototype plant are discussed.

A brief summary of some of the operating problems encountered is presented. Estimated annual operating costs (exclusive of maintenance and fixed charges) for a typical 500 MW power plant are presented.

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Flue Gas Desulfurization Symposium
Atlanta, Georgia
7 November 1974

DESCRIPTION AND OPERATION OF THE STONE & WEBSTER/IONICS SO_2 REMOVAL AND RECOVERY PILOT PLANT AT THE WISCONSIN ELECTRIC POWER COMPANY, VALLEY STATION, IN MILWAUKEE

1. INTRODUCTION

The Stone & Webster/Ionics SO_2 Removal and Recovery Process is based on absorption of sulfur dioxide in aqueous caustic which is subsequently regenerated in Ionics' SULFOMAT™ electrolytic cells (electrolyzers). This patented process is applicable to gaseous effluents from stationary power plants burning fuels containing sulfur and to tail gases from sulfur recovery plants, smelters and sulfuric acid plants.

The process consists of three essential steps arranged in a closed loop:

a. Sulfur dioxide (SO_2) is absorbed from flue gas in an aqueous caustic soda (NaOH)-sodium sulfate (Na_2SO_4) solution to produce aqueous sodium bisulfite ($NaHSO_3$) containing some sodium sulfite (Na_2SO_3).

b. This aqueous bisulfite-sulfite is mixed with dilute sulfuric acid resulting in formation of aqueous sodium sulfate and gaseous, wet sulfur dioxide. The latter can be recovered for sale as commercially pure SO_2, converted to commercial 66° Baume sulfuric acid or to elemental sulfur.

c. The aqueous sodium sulfate is converted by electroylsis into caustic soda and sulfuric acid. The caustic is recycled to Step 1; the sulfuric acid is recycled to Step 2.

The process can be summarized by the following reactions:

Step 1, Absorption

$$2\ NaOH + SO_2 \rightarrow Na_2SO_3 \qquad (1)$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow NaHSO_3 \qquad (2)$$

Step 2, Recovery

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2 \qquad (3)$$

$$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2SO_2 \qquad (4)$$

Step 3, Electrolytic Regeneration

$$2\ Na_2SO_4 + 6\ H_2O \rightarrow 4\ NaOH + 2H_2SO_4 + 2H_2 + O_2 \qquad (5)$$

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The primary side reactions are absorption of sulfur trioxide (SO_3) and the oxidation of sodium sulfite and/or bisulfite. Either reaction forms sodium sulfate directly from which sulfur oxides will not be released upon acidification. These side reactions, therefore, result in a sulfate ion increase in the system. Special electrolyzers are used to purge excess sulfate as pure, aqueous sulfuric acid (10% wt). The quantity of such acid is quite small compared to the amount of sulfur dioxide recovered. It may be used in the power plant,for example, for regeneration of ion exchange deionizers.

Under a joint program cosponsored by the Environmental Protection Agency and Wisconson Electric Power Company, the process has been tested at Wisconsin Electric's Valley Station in Milwaukee. Phase I of a planned three-phase demonstration program has been completed. It consisted of design, installation and operation of an integrated pilot plant, development of a full-scale electrolyzer system and preliminary design of a prototype system. It is planned that Phase II of the program will include design, procurement and installation of a prototype facility treating all the flue gas from one of the four 75 MW coal fired boilers at the station. Phase III would involve startup and long-term operation of the prototype facility. A flow scheme is shown in Figures 1 and 2 for the 75 MW plant.

2. PROCESS DESCRIPTION - PILOT PLANT

2.1 Absorption

Entering flue gas was cooled from $290^\circ \pm 20^\circ F$ to $120^\circ F$ by direct water quench in the bottom of the absorber, after which the gas was contacted with aqueous caustic containing sodium sulfate and about 8% sodium hydroxide. Flue gas was returned to the stack from the top of the absorber. The caustic was converted to an aqueous mixture of sodium bisulfite, sulfite and sulfate containing the SO_2 and SO_3 removed from the flue gas. Above the quench section there were three packed sections each 10 feet high, that contained 2 inch Tellerettes. For most of the test program the uppermost stage was used as a demister. Absorbent was recirculated around each absorbing stage.

The flue gas rate was varied from 4500 to about 9000 pounds per hour. SO_2 concentration varied from about 1000 to about 3600 ppm. Percentage removal varied from 85 to 95% at effluent gas concentrations containing 200-300-ppm SO_2.

2.2 Sulfur Dioxide Recovery

Prior to entering the stripper, net effluent from the absorber was reacted with the sulfuric acid-sodium sulfate mixture recycled from the

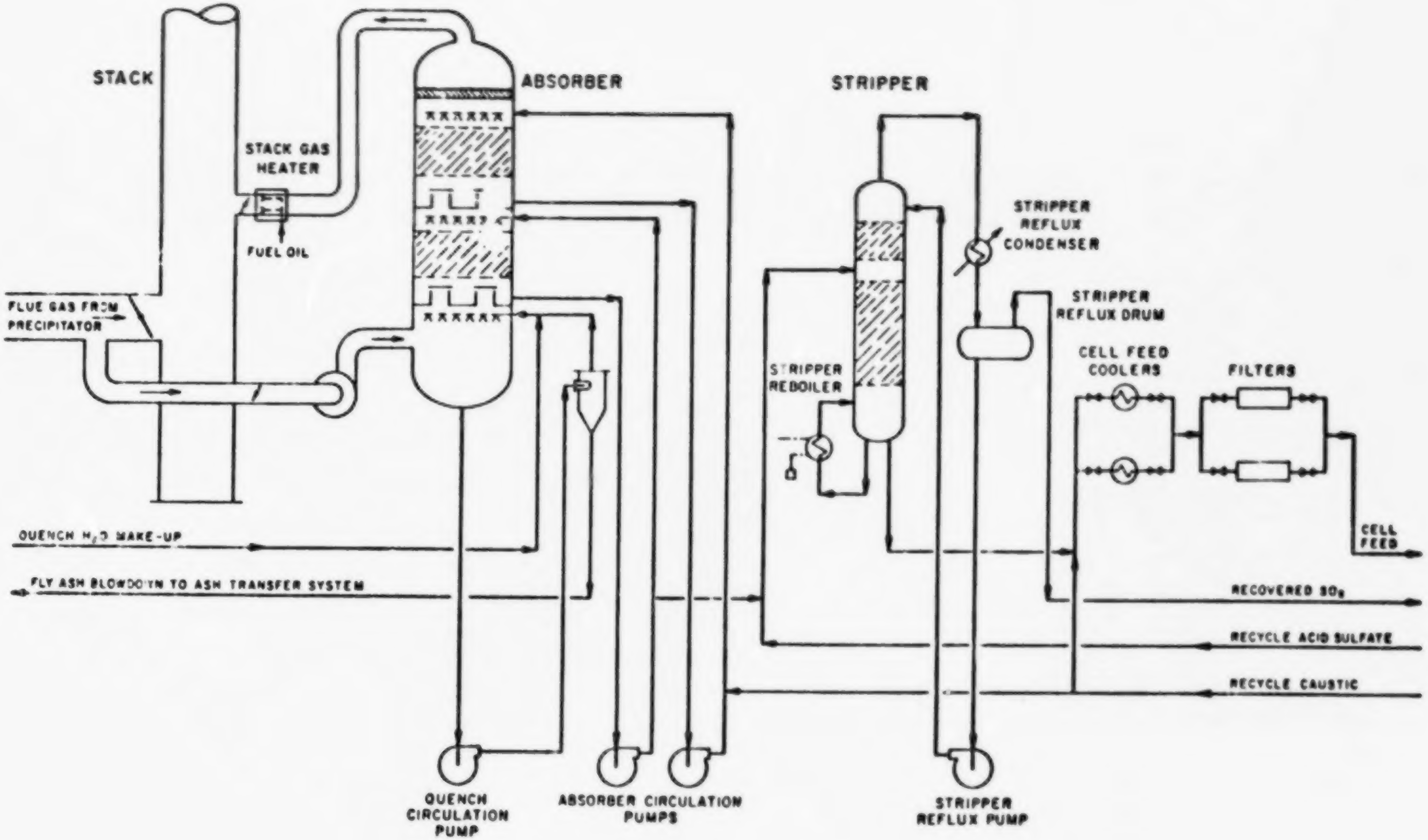

STACK
ABSORBER
STRIPPER
STACK GAS HEATER
FUEL OIL
FLUE GAS FROM PRECIPITATOR
STRIPPER REFLUX CONDENSER
STRIPPER REFLUX DRUM
STRIPPER REBOILER
CELL FEED COOLERS
FILTERS
CELL FEED
QUENCH H₂O MAKE-UP
FLY ASH BLOWDOWN TO ASH TRANSFER SYSTEM
RECOVERED SO₂
RECYCLE ACID SULFATE
RECYCLE CAUSTIC
QUENCH CIRCULATION PUMP
ABSORBER CIRCULATION PUMPS
STRIPPER REFLUX PUMP

Figure 1 SO_2 removal section.

Stone & Webster/Ionics SO_2 Removal & Recovery Process

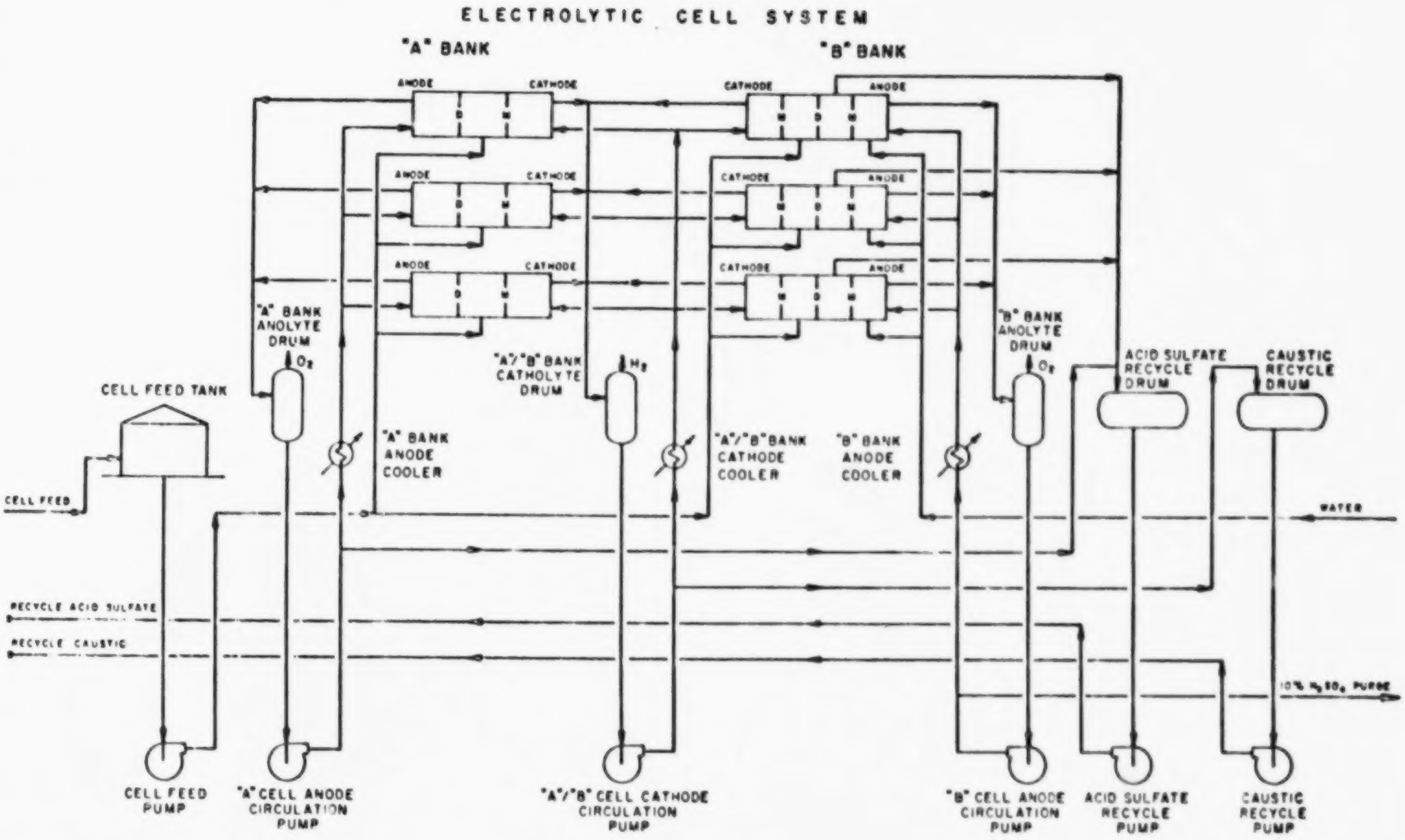

ELECTROLYTIC CELL SYSTEM
"A" BANK
"B" BANK
ANODE
CATHODE
ANODE
CATHODE
ANODE
CATHODE
CATHODE
ANODE
CATHODE
ANODE
CATHODE
ANODE
"A" BANK ANOLYTE DRUM
O_2
"A"/"B" BANK CATHOLYTE DRUM
H_2
"B" BANK ANOLYTE DRUM
O_2
ACID SULFATE RECYCLE DRUM
CAUSTIC RECYCLE DRUM
CELL FEED TANK
"A" BANK ANODE COOLER
"A"/"B" BANK CATHODE COOLER
"B" BANK ANODE COOLER
CELL FEED
WATER
RECYCLE ACID SULFATE
RECYCLE CAUSTIC
10% H_2SO_4 PURGE
CELL FEED PUMP
"A" CELL ANODE CIRCULATION PUMP
"A"/"B" CELL CATHODE CIRCULATION PUMP
"B" CELL ANODE CIRCULATION PUMP
ACID SULFATE RECYCLE PUMP
CAUSTIC RECYCLE PUMP

Figure 2 Regeneration system.

Stone & Webster Ionics SO_2 Removal & Recovery Process electrolyzers. The following reactions occurred in situ:

$$NaSO_3 + H_2SO_4 \longrightarrow H_2O + SO_2 + Na_2SO_4 \qquad (6)$$

$$2NaHSO_3 + H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + Na_2SO_4 \qquad (7)$$

The operating pressure was 10-15 psig. The reboiler temperature was 240-250°F. Recovered SO_2 in the stripper overhead was at a purity of 98%(vol) or greater. The stripper bottoms stream was controlled to a pH of about 3.5 and contained 50-100 ppm of dissolved SO_2.

2.3 Absorbent Regeneration and Oxidation Product Rejection

Aqueous sodium sulfate recovered from the stripper bottoms was adjusted to about pH 8.5 and hydrogen peroxide was added to precipitate iron as ferric hydroxide. After filtration, sodium sulfate was sent to two types of electrolyzers (as described in 2.4.3). In each type of electrolyzer, sodium hydroxide containing sodium sulfate was generated and was recycled to the absorber. A mixture of sodium sulfate and sulfuric acid was also generated and was recycled to the sulfur dioxide recovery step described above. Oxygen was generated as pure humid gas at the anodes of each electrolyzer. Pure humid hydrogen was generated at each cathode. Both gases were diluted with air and vented to atmosphere.

In the four-compartment ("B" type) electrolyzers, anode product was substantially pure, approximately 10% sulfuric acid equivalent in quantity to the SO_3 absorbed and SO_2 oxidized. In a commercial-scale plant this sulfuric acid could be withdrawn from the system for regeneration of mixed bed ion exchange deionizers, for marketing or for other disposal.

In the pilot plant the volume was small and the sulfuric acid was not recovered. During the initial operations of the pilot plant, the sulfuric acid sometimes contained substantial amounts of sodium sulfate due to upsets in cell operating conditions.

Sulfate ion so removed as dilute acid is a preferred method by which SO_3 contained in the entering flue gas plus SO_2 oxidized to sulfate in the absorber are removed from the system. The total amount of sulfate formed in the absorber determines the required number of four-compartment electrolyzers and the amount of acid produced. In the pilot plant, 36% of the electrolyzers had four compartments.

2.4 Technical Considerations

2.4.1 Absorption.

The overall process efficiency of sulfur dioxide removal from the flue gas is determined by three factors; they are:

a. The ratio of sodium sulfite to bisulfite in the net effluent liquor.

b. The amount of oxidation of sodium sulfite and/or bisulfite to sodium sulfate that occurs in the absorber, and

c. The amount of recycle caustic required for electrolyzer feed treatment.

Each of these factors can significantly affect the efficiency of the process.

The ratio of sodium sulfite to bisulfite is conveniently expressed in terms of the S/C ratio. The S/C ratio is defined as the ratio of moles of sulfur as sulfite and bisulfite to the moles of sodium associated with this sulfur. This ratio varies from 0.50 (100% sodium sulfite) to 1.00 (100% sodium bisulfite). The higher the S/C ratio, the lower the required amount of caustic to effect a given sulfur dioxide removal.

Oxidation is defined as the amount of sulfur dioxide absorbed as sodium sulfate compared to the total sulfur dioxide absorption. Absorption as sodium sulfate will consume two moles of caustic per mole of sulfur dioxide.

Sulfur dioxide absorbed as the sulfate will not be released by acidification with sulfuric acid and will result in a net sulfate ion increase in the system. The amount of oxidation will set the number of "B" cells required for removal of excess sulfate ion. "B" cells require more capital investment than "A" cells and consume slightly more power. This provides further incentive for minimizing oxidation. One of the primary goals of the test program was to study the influence of both operating and chemical parameters on the amount of oxidation.

The amount of recycle caustic required for feed liquor pH adjustment is determined by the extent to which acid addition at the stripper exceeds the stoichiometric requirement.

A. Caustic Utilization

Overall caustic utilization is defined as the ratio of the moles of sulfur dioxide absorbed per mole of caustic generated. A practical maximum caustic utilization is 0.90 moles of sulfur dioxide removed per mole of caustic generated. This is based upon a maximum S/C ratio of 0.925 in the absorber draw, a minimum caustic recycle of 3.2%, and assuming no oxidation.

The maximum S/C ratio is set by the equilibrium vapor pressure of SO_2 over the sodium sulfite-bisulfite-sulfate solution and is a function of the temperature and pressure of the system. The minimum caustic recycle required occurred at a stripper bottoms pH of about 3.50. Operation at this pH represents a balance between residual SO_2 in the stripper bottoms and the amount of excess acid added above the stoichiometric requirement.

The actual overall caustic utilization for the test program averaged about 0.78 or 86.9% of the practical maximum. This corresponds to an S/C ratio of 0.925, a caustic recycle of 5.0% and an oxidation level of 13.0%.

B. Oxidation

Oxidation levels in the absorber varied from 7 to 25% over the test program with the majority of measured values under 15%. The maximum uncertainty in this result was such that the best we could determine oxidation to was in the amount of 7%. That is, results indicating oxidation in the amount of 7% could also be interpreted as oxidation in the amount of 0%.

In general, oxidation was found to be affected by:

a. The amount of liquid recirculated to each stage. Higher rates increased oxidation.

b. The (S/C) of the effluent liquor. High S/C's favored lower oxidation.

c. The concentration of SO_2 in the inlet gas. Higher SO_2 partial pressure favored lower oxidation.

Additionally, varying the concentration of sodium sulfate did not appear to repress the amount of oxidation.

2.4.2 Sulfur Dioxide Recovery. The variable of primary concern in the stripping section is the minimum steam rate for a given SO_2 concentration in the bottoms. The concentration of SO_2 in the bottoms is determined by:

a. Stripping Steam Rate
b. Acidity
c. Temperature
d. Pressure
e. Number of Stripping Trays

There is an optimum bottoms concentration of SO_2 that is determined by economics. For example, recycling more acid will save steam by repressing the ionization of sulfurous acid. However, this also increases the downstream recycle caustic required for adjustment of the cell feed liquor acidity. Lowering the system pressure also enhances the stripping operation. However, if the bottoms temperature becomes too low, then heat exchange between feed and bottoms becomes impractical.

Heat exchange between feed and bottoms was not practiced in the pilot plant. Also, the reboiler and overhead condenser were generously sized making it difficult to control the stripping operation at low steam rates. Therefore, pilot plant results are not valid for extrapolation to a commercial scale.

For the SO_2-H_2O system at 10 psig and 50 ppm of SO_2 in the stripped solution and with heat economy, a stripping steam rate of 4 lb/lb SO_2 has been calculated. A minimum rate of about 2 lb/lb SO_2 is required for heating the feed stream.

However, the real situation is the system SO_2-H_2SO_4-Na_2SO_4-H_2O. The amount of ionized SO_2 in an acid salt solution should be less than in the SO_2-H_2O system and would result in easier stripping.

Some data available for the solubility of SO_2 in 0.10 N H_2SO_4 at 90°F indicates about a 50% decrease in SO_2 solubility. Thus, the minimum steam rate would probably be in the order of 3 lb/lb SO_2.

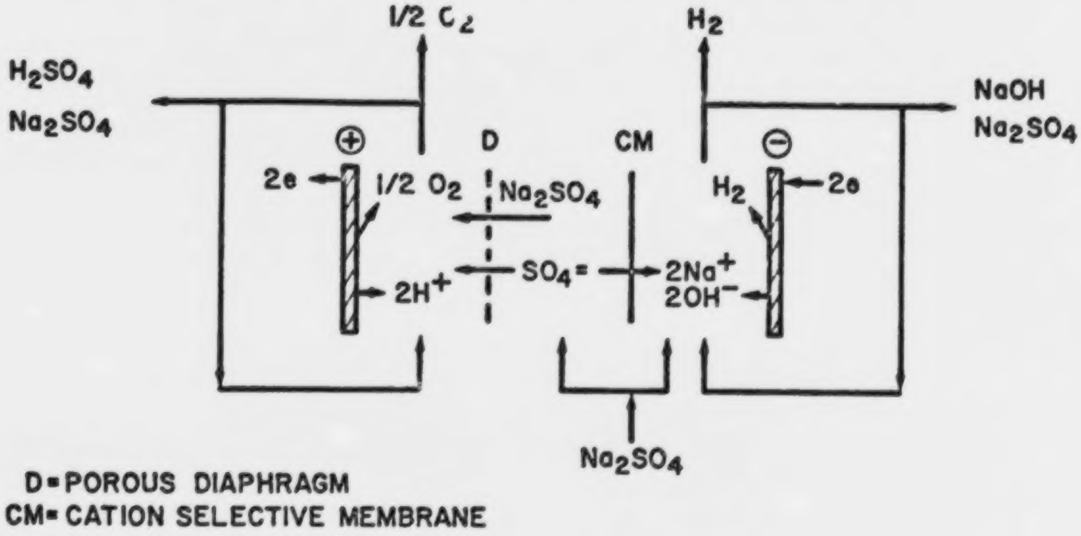
2.4.3 Absorbent Regeneration and Oxidation Production Rejection. The unique feature of the Stone & Webster/Ionics process is the electrolyzer system in which the caustic is regenerated. Reference has been made above to use of two different designs, a three-compartment electrolyzer and a four-compartment electrolyzer. The former is the basic design that converts sodium sulfate into sulfuric acid and caustic soda. The four-compartment design is the means by which excess sulfate is removed from the recirculating liquid system as pure, dilute sulfuric acid.

A schematic diagram of the three-compartment (Type "A") electrolyzer is shown in Figure 3. The main components are an anode, a microporous diaphragm, a cation-selective membrane and a cathode. These components are separated from each other by flow directing spacers which also provide required gasketing.

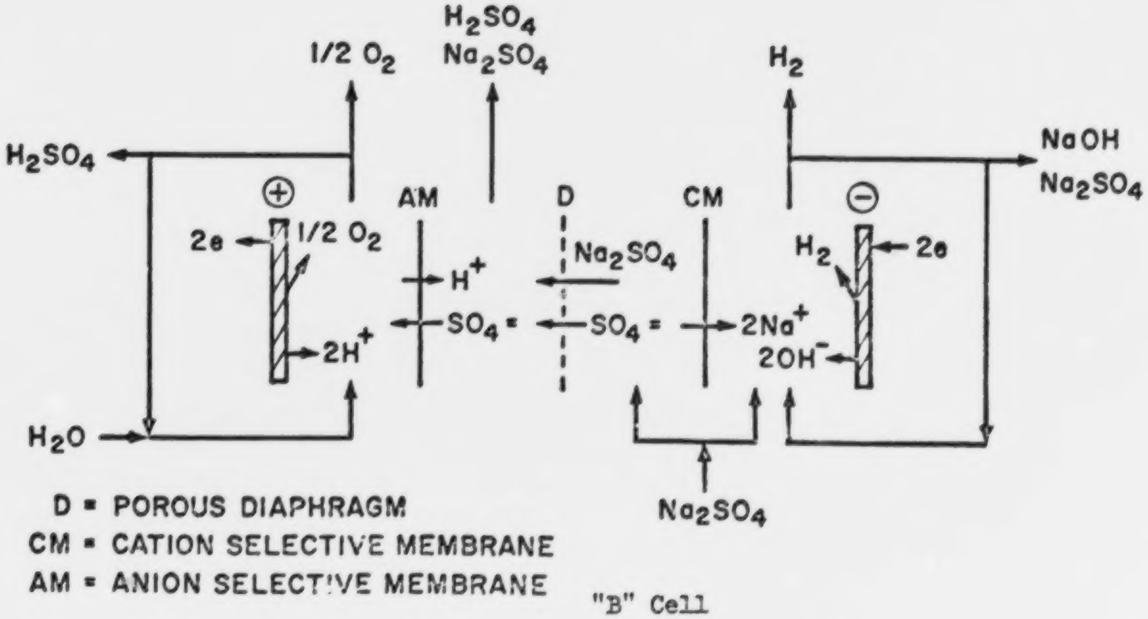
Stripped sodium sulfate solution from the stripper was cooled, pH adjusted to 8.5, and several ppm of hydrogen peroxide added to precipitate ferric hydroxide. The latter and other heavy metal oxide and hydroxides were removed by filtration. The sodium sulfate was fed to the central compartment of the electrolyzers at a concentration of about 20%. Sodium ions migrated through the cation-selective membrane toward the cathode under the influence of a direct current voltage impressed across the electrolyzer. At the cathode, water was electrolyzed to hydrogen gas and hydroxide anion:

$$H_2O + e^- \longrightarrow 1/2\ H_2 + OH^- \qquad (8)$$

The hydroxide anions were electrically balanced by sodium cations entering the cathode compartment through the cation selective membrane. The effluent catholyte consisted of NaOH plus Na_2SO_4, which after disengaging hydrogen was sent to a surge tank and then to the scrubber.


1/2 O2
H2
H2SO4
Na2SO4
NaOH
Na2SO4
⊕
D
CM
⊖
2e
1/2 O2
Na2SO4
H2
2e
2H+
SO4=
2Na+
2OH−
Na2SO4
D = POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE

"A" Cell


H2SO4
Na2SO4
1/2 O2
H2
H2SO4
NaOH
Na2SO4
⊕
AM
D
CM
⊖
2e
1/2 O2
H+
Na2SO4
H2
2e
2H+
SO4=
SO4=
2Na+
2OH−
H2O
Na2SO4
D = POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE
AM = ANION SELECTIVE MEMBRANE

"B" Cell

Figure 3 Schematic diagram of "A" and "B" electrolytic cells.

The function of the cation-selective membrane was to prevent physical mixing of the catholyte and center compartment feed streams. Essentially, only sodium cations from the center compartment pass through the membrane to combine with hydroxide anions produced at the cathode. Water may be fed to the catholyte compartment in sufficient quantity to produce 6 to 20% caustic. However, the Stone & Webster/ Ionics process is an essentially closed system. Therefore, to maintain water balance in the system it was necessary to feed recycled sodium sulfate solution to the catholyte compartment instead. This procedure does not introduce any problems and was the source of the sodium sulfate in the scrubber feed.

The center compartment feed passed through the microporous diaphragm, into the anode compartment. At the anode, water was electrolyzed to hydrogen cations and oxygen:

$$H_2O \longrightarrow \tfrac{1}{2}O_2\ (g) + 2H^+ + 2e^- \qquad (9)$$

The hydrogen cations combined with sulfate anions to form sulfuric acid. The diaphragm flow was designed to prevent hydrogen ions from migrating across the cation-selective membrane. Such flow must give enough linear velocity through the diaphragm to sweep hydrogen ions back into the anolyte compartment. The diaphragm should have an hydraulic resistance adequate to insure that such flow is substantially uniform over the entire surface. A flow which is sufficient to sweep back most of the hydrogen ions carries with it about half of the sodium in the center compartment. Thus, at the anode, only part of the sodium sulfate in the feed stream was electrolyzed to sulfuric acid. The anode product was therefore a mixed solution containing both sulfuric acid and sodium sulfate. This product was the dilute acid solution that was recycled to release SO_2 in the stripper.

In the four-compartment (Type "B") electrolyzers, a schematic diagram of which is presented in Figure 3, the reactions and operation of the catholyte compartment were exactly those described for three compartment electrolyzers. Catholyte effluents from both electrolyzer types were combined before being sent to the absorber. The center compartment feed flowed through the porous diaphragm, into the "mid-anolyte compartment", from which it was discharged from the electrolyzer. This stream contained some sulfuric acid due to the inability of the anion selective membrane completely to exclude hydrogen ion. The mid-anolyte effluent was combined with the anolyte stream from the three-compartment electrolyzers. The unique reactions of the four-compartment electrolyzer occurred at the anode, where water was electrolyzed to hydrogen cations and oxygen gas. These hydrogen cations combined with sulfate anions entering the anode compartment to form sulfuric acid. The function of the anion-selective membrane was to exclude sodium from the anode compartment while allowing sulfate to enter. It also, to a considerable extent, prevented hydrogen cations from leaving the anode compartment. Thus, the anode reactions permitted removing sulfate without losing sodium.

Each electrolyzer consisted of an anode, a cathode, at least one membrane, and one diaphragm with appropriate separators and internal flow distributors. A second membrane was placed between the diaphragm and the anode in the Type "B" electrolyzers. Fluid was internally manifolded and was in parallel. The electrolyzers were arranged into a number of modules within a single structural frame. The electrolyzers within a module were in parallel electrically and the modules were in series. The internal fluid manifolding was brought to headers in the frames. Headers were provided with quick-disconnect fittings to the electrolyzer fluid distribution and collection mains.

A large number of materials of construction have been tested in order to optimize life and performance of electrolyzer components. Both lead alloy and noble metal coated titanium anodes were tested. The latter were found to be more cost-effective. Preferred cathodes were nickel plated carbon steel and fluorcarbon fabric backings were preferable to acrylic backings for ion selective membranes. The life of the ion exchange resin component of such membranes appears to be entirely adequate. During the initial operations of the pilot program problems with other equipment in the system heavily loaded the electrolyzers with corrosion products and other atypical insoluble materials such as magnesium hydroxide and calcium carbonate. Such problems were eliminated in due course. We were pleased to observe that the electrolyzers readily returned to normal operation after such upsets.

Commercial-scale electrolyzer components, tested at Ionics in Watertown, Mass., were designed to be even more rugged. This scaling up has been accomplished with a reduction in electrical energy consumption. The specifications of the electrolyzers are essentially as follows:

	"A" Cells	"B" Cells
Effective area per cell	5 sq. ft.	5 sq. ft.
Operating Temperature	160°F	160°F
Effective Cell Height, inches	20	20
Interelectrode Distance, inches	0.317	0.345
Current Efficiency, overall	85%	85%
Current Efficiency, pure acid	----	40%

2.5 Operating Experience

The vast majority of the operational problems experienced at the test site were mechanical in nature and typical of any pilot plant operation. Once these problems were resolved the process had an overall operation availability of greater than 90% during the latter stages of the test program.

Forced draft fan vibrations were a frequent cause for shutdown. This was finally traced to a buildup of acid sludge on the blades occurring only at gas inlet temperatures below 225°F. Water washing the fan blades and flue gas temperature control reduced the vibrational problems to a manageable level.

During the initial phases of the test program, the extent of feed liquor cleanup required for smooth electrolyzer operation was not well understood. Improper liquor cleanup caused a number of shutdowns until an adequate system was installed.

Pressure control on the stripper overhead was hampered by sulfur dioxide hydrate formation in the instrument lines, the flow measuring orifice, condenser tubes, or a combination of all three. This problem is correctable by maintaining temperatures above 60°F at all points in the system.

Absorption liquor entrainment losses were a problem when operating with three packed stages. The high pressure drop nozzles initially installed in the liquor recirculation lines produced a fine atomizing spray which in combination with the relatively high gas velocities was responsible for the entrainment. Replacement of the spray nozzles and operating with the third packed stage as a demister corrected the problem.

The system suffered from a continual water loss throughout the test program. This loss was traced to the evaporation of water from the process liquids due to incomplete saturation of the flue gases in the water quench section. This loss was in addition to the known water of decomposition required for the electrolysis operation. A reasonably constant feed liquor density and purity is required for good cell voltage control, hence continuous water addition to the cell feed liquor is necessary.

3. 75 MW PROTOTYPE FACILITY

A 75 MW prototype facility has been designed. It is proposed that it be installed at the Valley plant of Wisconsin Electric Power Company.

The basis of design is:

a. Process all the flue gas from one 75 MW boiler at 100% load factor, approximately 260,000 ACFM at 320°F.

b. Based on statistical analyses of recent coal burn, the plant will be designed to remove an average of 3100 pounds of SO_2 per hour on a continuous basis.

c. Sufficient "B" Type four-compartment electrolyzers will be used to provide for a maximum oxidation quantity in the amount of 15%.

d. Flue gas to be desulfurized by a minimum of 90%.

e. 1152 "A" Type electrolyzers will be used having a total active area of 5760 square feet. 384 "B" Type electrolyzers will be used having a total active area of 1920 square feet.

4.0 PROCESS ECONOMICS

Since many large boilers supplying steam for power generation have capacities of the order of 500 MW, we have developed operating costs for a 500 MW plant instead of the smaller 75 MW plant proposed for Milwaukee. We believe these costs are more representative of the average power plant installation. Costs of utilities do not necessarily reflect WEPCO costs, but are those generally used in assessing costs of competitive processes.

Estimated annual operating costs, excluding fixed charges and maintenance, are shown in Tables 1 and 2 for a coal fired plant assuming 3.5% S coal, 90% SO_2 removal and 80% boiler load factor. Table 1 assumes that the stack gas is reheated using the hydrogen generated by the electrolyzers and low sulfur No. 6 fuel oil. Table 2 assumes no stack gas reheat, but assumes the hydrogen generated is burned for its heating value.

Fixed charges for the plant have not been included for two reasons. First, because of the present high rate of inflation affecting equipment, materials and labor costs, capital cost can be made to vary depending on the amount of optimism or conservatism applied to the plant cost estimate.

Second, there is still not agreement in the industry on the annual fixed charge rate required to amortize the capital investment of pollution control facilities. Typically, utilities write off capital for generating facilities at 14% per year. Such a policy has the effect of increasing annual pollution control charges compared to other methods of financing. For example, if the plant were instead financed with 20-year 9% bonds, annual debt service would be 11%, not 14%. On the other hand, if one took full advantage of special financing permitted for pollution control facilities, then the effective annual capital charge would be only about 7%. Such a rate assumes:

a. 100% financing by industrial revenue bonds at 6% interest

b. Straight line pay-backs of principal

c. Accelerated depreciation under Internal Revenue Service

d. 7% discount rate for all cash flows

TABLE 1 APPROXIMATE ANNUAL OPERATING COST WITH STACK GAS REHEAT STONE & WEBSTER/IONICS SO_2 REMOVAL PROCESS

Basis: 500 MW; 1,355,000 tons per year of 3.5% S Coal;
80% Load Factor; 90% SO_2 Removal

Utilities & Chemicals	Quantity	Unit Price	Total
Soda Ash	260 T/Y	$ 60	$ 15,600
Hydrogen Peroxide	260 T/Y	$ 300	78,000
Filter Aid	---	---	62,400
Electricity-Electrolyzers	27,500 KW	11 mils	2,115,000
Electricity-Auxiliaries	10,600 KW	11 mils	816,000
Steam (100 psig)	68,000 lbs/hr	$ 1.50/1000 lbs	715,000
Condensate	112 GPM	$ 0.30/1000 gals	14,000
Cooling Water	8,000 GPM	$ 0.03/1000 gals	101,000
No. 6 Fuel Oil, Low S	6 bbl/hr	$ 12.10 bbl/hr	503,000
Subtotal, Utilities & Chemicals			$ 4,420,000
Operating Labor	3/shift	$ 11/hr	$ 290,000
Administration, Supervision and Laboratory	---	---	$ 150,000
Credit for S in SO_2 (Includes credit for 10% sulfuric acid at sulfur value)	38,000 LT/yr	$15/LT Sulfur	-$ 570,000
Total Operating Cost (excluding maintenance)			$ 4,290,000
Cost per KWH, (3.5×10^9 KWH)			1.2 mils
Cost per Ton of Coal (1,355,000 tons)			$ 3.17

TABLE 2 APPROXIMATE ANNUAL OPERATING COST WITHOUT STACK GAS REHEAT STONE & WEBSTER/IONICS SO_2 REMOVAL PROCESS

Basis: 500 MW, 1,355,000 tons per year of 3.5% S Coal;
80% Load Factor; 90% SO_2 Removal

Utilities & Chemicals	Quantity	Unit Price	Total
Soda Ash	260 T/Y	$ 60	$ 15,600
Hydrogen Peroxide	260 T/Y	$ 300	78,000
Filter Aid	---	---	62,400
Electricity-Electrolyzers	27,500 KW	11 mils	2,115,000
Electricity-Auxiliaries	10,600 KW	11 mils	816,000
Steam (100 psig)	68,000 lb/hr	$ 1.50/1000 lbs	715,000
Condensate	112 GPM	$ 0.30/1000 gals	14,100
Cooling Water	8,000 GPM	$ 0.03/1000 gals	101,000
Subtotal, Utilities & Chemicals			$ 3,917,000
Operating Labor	3/shift	$11/hr	$ 290,000
Administration, Supervision and Laboratory	---	---	$ 150,000
Credit for S in SO_2 (Includes credit for 10% sulfuric acid at sulfur value)	38,000 LT/yr	$15/LT Sulfur	-$ 570,000
Credit for H_2	27 MM BTU/hr	$1.59/MMBTU (LHV)	-$ 300,000
Total Operating Cost (excluding maintenance)			$ 3,487,000
Cost per KWH, ($3.5\ 10^9$ KWH)			1.0 mils
Cost per Ton of Coal (1,355,000 tons)			$ 2.57

Such industrial revenue bonds and accelerated depreciation have become very popular for financing pollution control plants.

5. CONCLUSION

Operation of the WEPCO pilot plant of the electrolytically regenerated SO_2 removal and recovery process has been completed. The process has been shown to be technically feasible and it has been demonstrated that process reliability can be designed into the process to maintain the continuity of operation required by the power generation industries.

The electrolyzers (electrolytic regeneration cells) performed somewhat better than expectations and were found to be surprisingly forgiving of upsets in ancillary systems and components. Problems with some components and materials of construction in the ancillary systems were found and solved during the pilot program.

Preliminary design of a 75 MW prototype system has been completed. Experience from the pilot plant has been incorporated and it is believed that the prototype will demonstrate the reliability required for power plant operation.

CALSOX SYSTEM DEVELOPMENT PROGRAM
PRESENTED AT THE
EPA FLUE GAS DESULFURIZATION SYMPOSIUM
November 4 - 7, 1974 — Atlanta, Georgia

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ABSTRACT

The CALSOX system was developed by Monsanto to overcome the scaling problems encountered by systems scrubbing SO_2 bearing gases with lime/limestone slurries. The CALSOX system removes the SO_2 from the gas by absorption in an aqueous ethanolamine solution, using a relatively simple gas/liquid contactor. Removal of the sulfur values from solution occurs externally of the contactor by precipitation with lime in a system designed specifically for this purpose. After separation of the insoluble calcium salts by filtration, the regenerated absorbent solution is returned to the system. Thus, by minimizing precipitable calcium ions in the gas/liquid contactor, scaling is prevented.

A 3,000 acfm pilot unit began operation in February 1973 in a joint program with Indianapolis Power & Light Company and continued until the end of October 1973. Design criteria originally established for the process included:

SO_2 removal — 90% minimum
Particulate emission — .02 grains per scf maximum
Calcium oxide usage — 120% stoichiometric maximum
Ethanolamine usage — 2.0 lbs./Mwhr.

The performance experienced during operation of the pilot plant system exceeded all the preceding criteria. The absence of scaling and pluggage in the gas scrubbing equipment was demonstrated during sustained operation; however, some problems did occur in the liquid and gas handling equipment which will be discussed in the paper.

The process design for a 125 Mw demonstration plant has been completed and a detailed capital and operating estimate prepared.

CALSOX SYSTEM DEVELOPMENT PROGRAM
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PROCESS CHEMISTRY

The CALSOX[1] system presents a new concept in SO_2 scrubbing of boiler flue gases. The flue gas is scrubbed with an aqueous ethanolamine solution which absorbs the SO_2, which when precipitated with lime produces calcium sulfite and calcium sulfate. Two of the unique concepts of the CALSOX system are the use of the ethanolamine absorption solution and the two step regeneration which prevents calcium scaling in the absorber.

Ethanolamine was chosen as the alkaline agent for absorption because it allows complete regeneration with lime. Figure 1 shows the ethanolamine neutralization curve for absorption of SO_2. As indicated on this curve the original pH of an aqueous ethanolamine solution is 11.3. Lime has a very high solubility over the entire neutralization range. All the lime added will be utilized in precipitating sulfur species up to the neutralization point.

After precipitation of the sulfur species as calcium sulfite and calcium sulfate, the resulting solution will have an equilibrium concentration of calcium and sulfate ions, approximately .02 molar. This concentration of calcium ions is greater than can be tolerated in the absorption system without the potential for scaling as a result of calcium sulfite precipitation. For this reason the two step regeneration is used to lower the calcium ion to the calcium sulfite solubility and thereby eliminate the possibility of scaling in the absorption step. After complete regeneration with lime the solution is mixed with the scrubber return liquor in a reaction tank and the calcium ion is precipitated as calcium sulfite. The clear liquor from this step is then used in the scrubbing operation.

The CALSOX process that applies this chemistry is presented in Figure 2. Flue gas from the boiler's existing induced draft fan flows to a booster blower which directs the gas to a single stage absorption system for removal of the SO_2. The cleaned gas is then reheated, if required, to minimize steam plume formation, and then goes to the stack. The rate of SO_2 removal can be controlled by changing the operating pH of the absorber.

The SO_2 rich absorbent from the absorber then flows to a two step regeneration system where the sulfite and sulfate ions are precipitated as the calcium salts and the regenerated absorbent is returned to the system. In the first step, part of the sulfite is precipitated as calcium sulfite thereby lowering the soluble calcium level to below 50 parts per million and eliminating the possibility of scaling in the absorber. In the second step the remaining sulfate and sulfite ions are precipitated with lime; the calcium addition is controlled by pH. Lime slurry is prepared by feeding quicklime from a storage silo and absorbent solution from the regeneration system to a conventional lime slaker. The slaked lime slurry is introduced on demand to the second regeneration reactor.

The underflow slurry of calcium sulfite and sulfate crystals is fed from the thickener to a vacuum filter for dewatering and washing. The amount of wash water is controlled to equal the amount of water lost by evaporation in the adiabatic cooling of the gas stream in the absorber. The filtrate and wash water are returned to the process providing a closed loop system. The separation of the absorption and regeneration steps and the buffering capacity of the ethanolamine solution provide for good control of the entire system.

PILOT PLANT PROGRAM

In April 1972, Indianapolis Power & Light Company and Monsanto entered into a joint program on the design, construction and operation of a 3,000 acfm pilot unit. This pilot unit was installed at the Elmer W. Stout Generating Station in Indianapolis, Indiana and began operating in February 1973. The operating and testing program continued until the end of October 1973, at which time it was concluded that sufficient information had been obtained for the design of a demonstration unit in the 100 - 125 Mw range. The design criteria originally established for the process included: SO_2 removal, 90% minimum; particulate emission, 0.02 grains per scf maximum; calcium oxide usage, 120% stoichiometric maximum; absorbent usage, 2 lbs. per megawatt hour maximum. Performance experienced during sustained operation of the pilot plant system exceeded all the preceding criteria.

Figure 3 is a flow diagram of the pilot plant. The pilot plant as constructed at Indianapolis Power & Light Company differed from the process description presented in Figure 2 in three areas. In the pilot plant, gas was to be taken both before and after the electrostatic precipitator. Therefore, a scrubber was installed ahead of the absorber for particulate removal since it was not known how much particulate the absorber could tolerate. The second change was that the pilot plant used an ID fan instead of an FD fan. The fan was a 3600 rpm overhung fan installed between the absorber and the reheater. The other change in the pilot plant from the process design shown in Figure 2 is the use of reactor clarifiers instead of reactors separated from thickeners. These are the areas of importance in the discussion of the problems encountered in the pilot plant and the resolutions that will be used in the full scale design.

A Ventri Rod[2] scrubber was used in the pilot plant for particulate removal. It was operated at 10 inches water pressure drop with a liquid to gas (L/G) ratio of 13.5 gallons per thousand standard cubic feet. When the gas stream was taken before the electrostatic precipitator (but after a mechanical collector) the overall average ash loading was 0.86 grains per standard cubic foot. The average outlet loading of the scrubber was 0.036 grains per standard cubic foot. This represents approximately 96% removal of the fly ash. There was additional fly ash removal in the cross flow absorber. The average outlet loading from the absorber was 0.004 grains per standard cubic foot. The fly ash removal across the absorber alone was approximately 87%.

The absorber was able to achieve 90% SO_2 removal under all conditions even when the inlet SO_2 dropped to as low as 1500 parts per million. This was with the absorber operating at an L/G ratio of 25 gallons per thousand standard cubic feet. When the liquid across the absorber was reduced to 12 gallons per thousand standard cubic feet the absorption efficiency was approximately 80%. The lime utilization fluctuated in the regeneration reactor as a result of fluctuation in the pH control. The average lime utilization was approximately 102% of stoichiometric, significantly better than the target of 120%. Washing efficiency was good on the horizontal vacuum filter. The absorbent utilization, represented by loss in the cake, averaged 0.5% in the dry cake, which is equivalent to 0.6 pounds per megawatt hour, a significant improvement over the target of 2 pounds per megawatt hour.

The operating program for the pilot plant was divided into three phases. Phase I was the start-up and shake-down period from February 6 to March 31, during this period the unit operated approximately 75% of the time. A summary of the operation is presented in Table 1. In general, the problems were normal to start-up and shakedown. There was a carbon steel valve that was incorrectly installed and had to be replaced with a stainless valve. There were other operating problems associated with learning the peculiarities of the system. There was a major outage associated with repair of the ID fan. It was cleaned and balanced and one of the bearings was replaced.

A major change that came out of the operation in Phase I was the relocation of the lime slurry system. In the original pilot plant, lime as calcium hydroxide was slurried on the first level and then pumped by a Moyno[3] pump up to the reaction chamber in the reactor clarifier. There were several problems associated with this system. The package unit purchased had a 5 minute residence time in the slurry tank. This was too short a time and provided excessive scaling. Furthermore, scaling occurred in the Moyno pump and in the line up to the reaction zone. The scale built up as small pieces of material that would eventually plug the line since there was insufficient fluid velocity to keep the line clean. Recirculation was attempted but was unsuccessful. During the period of April 1 - 16, the lime slurry system was relocated to the second level where it could gravity overflow into the reactor clarifier. Clear liquor from the clarifier overflow was pumped continuously through the slurry chamber and on demand from the pH controller lime was added. Excellent automatic pH control was maintained in the absorber and recycle clarifier; however, significant problems were encountered with scaling on the pH electrodes in the reaction chamber of the reactor clarifier. This was not successfully corrected during Phase I and the majority of operation during this period was on manual control. Later improvements allowed better monitoring. Fortunately, the system had a very large capacity and the pH did not change rapidly.

Deposits on the ID fan were handled by the introduction of an intermittent water wash into the inlet of the ID fan, 2 gpm for a period of two minutes every two hours. This was sufficient to keep the majority of the deposits off the fan and did allow it to operate without excessive vibration.

Table 2 is a summary of Phase II operation. The objective of Phase II was to demonstrate on-stream operability. The system was to be run at a steady state condition for a period of at least 30 days continuous operation. The period covered is from April 17 through May 29. During this period the unit operated with a 99.7% on-stream time. The outages were associated with electrical malfunctions, primarily the control panel which had a faulty circuit breaker. This could not be replaced until the unit was taken off line, so the unit was continued in operation with this problem. In this test period, the unit was considered on-stream if the absorber was handling flue gas and removing SO_2 to the code limit. Maintenance was required on the lime handling and filter systems, but these did not affect the operation of the absorber. One of the important features of the CALSOX system is the ability to have the lime handling and filter operations off stream for periods of up to 8 hours without affecting the rest of the plant. This capability is associated with the large absorption capacity of the ethanolamine solution, and of course the storage capacity of the reactor clarifier (thickener).

The major process problem encountered in Phase II was pluggage of the reactor underflow line from the reactor clarifier to the filter. Steady state flow in this line was approximately 0.5 gallons per minute. At this flow the linear velocity through the line was very low. A Moyno pump was used and in general this supplied satisfactory control of the flow of the material, but any accumulation of large chunks would block the underflow line. It was also found that the scrapers on the rake in the clarifier zone had too much clearance and would allow accumulation of compacted sludge in the bottom of the clarifier. This compacted material would break off in large pieces from the wall and plug the underflow to the filter. This problem was alleviated by the installation of neoprene wipers on the ends of the clarifier scrapers and the relocation of the discharge opening. In addition, the sludge level was maintained at a fairly low value during most of the operation to eliminate the possibility of compacted material. The slurry was also recycled continuously when it was not being fed to the filter. The filter was oversized for the total slurry generated and it could not be operated continuously. This caused some problems at first in maintaining stable filter operation, but with more experience it was possible to start up and shut down the filter without significant problems.

In Phase III the operation of each unit of equipment was studied to determine its optimum performance capabilities and to provide accurate information for sizing of a full scale demonstration plant. This period of operation covered from June 9 through October 14. Included was a 3 week period when the IPALCO personnel operated the plant. There were several outages during Phase III associated with rearrangement of equipment and special testing, but the majority of the outages were caused by operating problems with the ID fan. In Table 3 is presented the history of the ID fan operation during Phase III. During the early part of Phase III the intermittent washing operation of the ID fan was discontinued because of unsatisfactory results.

At the end of Phase II a build up of vibration was noted in the ID fan; it was removed from its housing, sandblasted, checked for cracks, balanced and reinstalled. When reinstalled, a continuous washing operation was attempted. The result was disastrous as the fan blades corroded completely through and the fan wheel separated.

Because of delivery time of a new fan wheel, a replacement ID fan was obtained. During the down time to install the replacement fan, hot gas recirculation was installed to allow the reheated gas from the exit of the reheater to be recirculated to the inlet of the blower. This was not completely successful but was continued throughout the remainder of the operation. The inlet temperature to the fan was maintained at 160°F or higher in an attempt to minimize the deposition of particles on the fan blades.

After a replacement wheel for the original fan was obtained it was epoxy coated and reinstalled. The washing program established was to wash for 15 seconds with hot water every 2 hours. It was found after approximately one month operation that the epoxy coating was beginning to flake off and that some fly ash was depositing on the fan. Figure 4 shows the condition of the fan wheel. In Figure 5 it can be seen that not only is fly ash present, but also some traces of crystalline calcium sulfate material. The next fan coating attempted was a 15 mil neoprene coating. This was not successful as the neoprene shredded after a very short period of operation. The last coating attempted was epoxy and the time between washing was lengthened to 15 seconds every 4 hours. The final inspection after three weeks of operation indicated that the fan wheel was in good condition and very clean. Nevertheless, in future plant installations, it is proposed that an FD fan will be used to eliminate the problems associated with an ID fan. The FD fan concept was not demonstrated in the pilot plant; however, it has been well proven in other applications.

During the third phase of the pilot plant operation, the unit was on-stream approximately 72% of the time. At the end of the third phase of operation it was concluded that sufficient information had been obtained for the design of a large scale demonstration plant. In November 1973, a program was entered into between Monsanto and Indianapolis Power & Light for the design and cost estimation of a 125 megawatt demonstration plant.

LANDFILL STUDIES

During the pilot plant operation, filter cake from the vacuum filter was used in landfill studies at the IPALCO site. A schematic of the landfill test arrangement is shown in Figure 6. One inch flexible plastic tubing was set into the ground at different levels and the leachate material was collected from these tubes periodically. Four different test plots were set up: 1) A control site with no cake, 2) A cakefill, 3) A cake fly ash fill where the cake was mixed approximately 50% with fly ash, and 4) An activated sewage sludge treated cakefill. In order to increase the amount of data obtained, the sites were irrigated with fly ash pond water over a period of one year. In this way the landfill sites were exposed to the equivalent of two years of normal rainfall for the Indianapolis area over a single year of seasonal cycles. During the exposure leachate samples were taken at different depths below the fill material. After exposure, landfill plot corings were taken. Additional studies on biodegradation of leachate, solubilization of metal ions and cake and leachate toxicities were carried out. Figure 7 shows a photo micrograph of fresh cake taken from the filter belt, and Figure 8 shows typical landfill material after exposure to one year of seasonal cycles. One of the major findings of the landfill studies is that the cake from the CALSOX system reduces the permeation rates through normal soil. Some of the general conclusions obtained from the landfill studies is that the pH of the leachate is neutral to slightly basic. The soluble salts level in the cake leachate is of an order two to four times greater than was found in the control, but the soluble salts level is still below the potable water standards. Fly ash addition most significantly affects the dissolved chloride ion concentration in the leachate. The trace element levels below the fill were not significantly affected by the cake.

The use of sewage sludge on the surface of site four resulted in a high organism at the time of the cake landfilling. This represents the most severe condition for biological activity encountered in any normal landfill. The presence of many varieties of organisms allowed for selective growth in the landfill media. This resulted in observation of a process which would normally take very long periods to establish in the absence of the organism treatment. The leachate supports organism growth below the ground resulting in higher organic carbon loading in the leachate. The organisms in the ground appear to metabolize leached sulfur compounds producing thio compounds and possibly some sulfide ion. Separate studies were undertaken to determine some of the additional parameters associated with landfilling of the cake. It was found that the leachate is readily biodegradable under aerobic conditions and probably also under anaerobic conditions. It was found that the leachate material did not significantly affect the solubilization of metal ions in the specific cases studied: nickel, copper, cadmium and lead. In all cases at pH around 11 the solubility in the leachate was less than in an aqueous solution whereas in neutral solution the solubility in the leachate was slightly higher than in the aqueous solution. It was also found that the cake and cake leachate are relatively inert and have no significant toxicity. This was measured in the normal terms of the irritation properties to laboratory animals and acute toxicity by aquatic tests with both bluegills and trout.

DESIGN AND ESTIMATION OF THE 125 Mw DEMONSTRATION PLANT

As a result of a successful completion of a pilot plant operation, it was jointly agreed between Indianapolis Power & Light Company and Monsanto Enviro-Chem Systems that a demonstration plant of approximately 125 megawatts would be designed using CALSOX engineering and a cost estimate prepared for a CALSOX unit that would handle approximately one-fourth the flue gas from the No. 7 unit of the Elmer W. Stout Generating Station in Indianapolis. Figure

9 shows the CALSOX system Plot Plan at IPALCO. Basic design criteria for the plant included a new independent stack to handle the flue gas from the plant, use of pond water to slurry the cake to landfill area and use of a railway system for delivery of lime and the ethanolamine absorbent.

The demonstration plant design incorporated the changes that were developed during the pilot plant operation; namely, the relocation of the booster blower from an induced draft to a forced draft and the installation of the lime slurry facilities at such a level that it would allow for gravity overflow into the reactor. In addition, since this unit would be receiving the gas after the electrostatic precipitator, only the absorber section was included as a scrubber module was not required. Flue gas reheat (if required) will be by the mixing of heated ambient air with the flue gas stream providing the capability of approximately 50°F of reheat. A testing program would be carried out to determine any need for reheat.

An additional change in the demonstration plant is that the reaction zones will no longer be integral with the reactor clarifiers as was used in the pilot plant. Separate reactor vessels will be installed so that a good level of agitation can be provided in the continuous stirred tank reactors. This should improve agitation and give a better degree of reaction completion than was found in the pilot plant. The reactor clarifier will be replaced with a heavy duty thickener to better handle the sludge. Duplicate lime slaking facilities are also included in the plant design to provide for maximum reliability.

The cost of the 125 megawatt demonstration plant, including escalation during the construction period, is estimated at about $9-million which is approximately $72 per kilowatt installed capacity. The operating costs, taking advantage of the raw material performance demonstrated by the pilot plant, is estimated to be about 3.0 mills per kilowatt hour. Figure 10 shows the Estimated Operating Costs.

SUMMARY

The feasibility of the CALSOX process has been demonstrated in pilot operation. The concept of absorbing SO_2 with ethanolamine and avoiding scaling in the gas handling equipment is a very forward step to a reliable system. The low liquid to gas ratio should reduce capital and operating costs. The buffered absorbent will allow flexibility in the system and offer easier pH control. We look forward to the future when the development program on CALSOX is more complete and a full scale demonstration unit is in operation.

TABLE 1

Summary of Operation
Phase 1 Start-Up

PERIOD	OPERATING HOURS	OUTAGE HOURS	OUTAGE
FEB. 6 — FEB. 8	53	4	FORCED OUTAGE — PLUGGAGE OF ABSORBER SPRAY NOZZLES
FEB. 9 — FEB. 18	—0—		SCHEDULED OUTAGE #5 BOILER SEMI-ANNUAL MAINTENANCE
FEB. 19 — FEB. 28	221	4	FORCED OUTAGE — REPAIR SCRUBBER FLOW CONTROL VALVE; REPAIR ABSORBER PIPING
MARCH 1 — MARCH 2	—0—	67	FORCED OUTAGE — REPLACE SCRUBBER FLOW CONTROL VALVE WITH STAINLESS STEEL
MARCH 3 — MARCH 10	121	32	FLUE GAS FLOW CONTROL REPAIR; INSTRUMENT AIR REPAIR; ID FAN REPAIR
MARCH 10 — MARCH 14	—0—	96	FORCED OUTAGE — CLEAN AND BALANCE ID FAN; REPLACE BEARING
MARCH 14 — MARCH 31	395	7	PLUGGAGE IN REACTOR OVERFLOW LINE; FOULING IN ABSORBER PUMP
APRIL 1 — APRIL 16	—0—		DOWN FOR EQUIPMENT MODIFICATION

TABLE 2

Summary of Operation Phase II
On-Stream Operability

APRIL 17 TO MAY 29

TOTAL DAYS OPERATED — 42.33

TOTAL HOURS OPERATED — 1012.34

TOTAL HOURS OUTAGE — 2.66

PERCENT ON-STREAM — 99.7

OUTAGES

DATE	TIME	DURATION HOURS	REASON
4-21-73	1500-1630	1.5	ID FAN OFF — SCRUBBER PUMP DRY — SCRUBBER RECIRCULATION STOPPED. CAUSE — UNKNOWN
4-24-73	0140-0210 0425-0445	.83	POWER TO CONTROL PANEL OFF — FLUE GAS FLOW FLUCTUATION. CAUSE — UNKNOWN (ELECTRICAL STORM).
4-29-73	2300-2320	.33	POWER TO CONTROL PANEL OFF — RESET BREAKERS — RESTART FAN. CAUSE — UNKNOWN.

TABLE 3

Phase III Parametric Studies
ID Fan Operation

DATE	UNIT	COATING	WASHING	COMMENTS
6-9 TO 6-16	ORIGINAL FAN	NONE	CONTINUOUS 0.5 GPM	CATASTROPHIC CORROSION
6-28 TO 7-13	REPLACEMENT FAN	NONE	NONE	FLY ASH DEPOSITS
7-19 TO 8-2	REPLACEMENT FAN	NONE	NONE	FLY ASH AND ABSORBENT DEPOSITS — INSTALLED HOT GAS RECIRCULATION TO BLOWER INLET
8-5 TO 9-7	ORIGINAL FAN	1 MIL EPOXY	15 SEC./2 HRS.	EPOXY FLAKED OFF — FLY ASH DEPOSITS
9-14 TO 9-25	ORIGINAL FAN	15 MILS NEOPRENE	15 SEC./2 HRS.	NEOPRENE SHREDDED
9-29 TO 10-14	ORIGINAL FAN	1 MIL SPECIAL EPOXY	15 SEC./4 HRS.	FINAL INSPECTION SHOWED VERY CLEAN WHEEL.

FIGURE 1

Ethanolamine Neutralization Curve

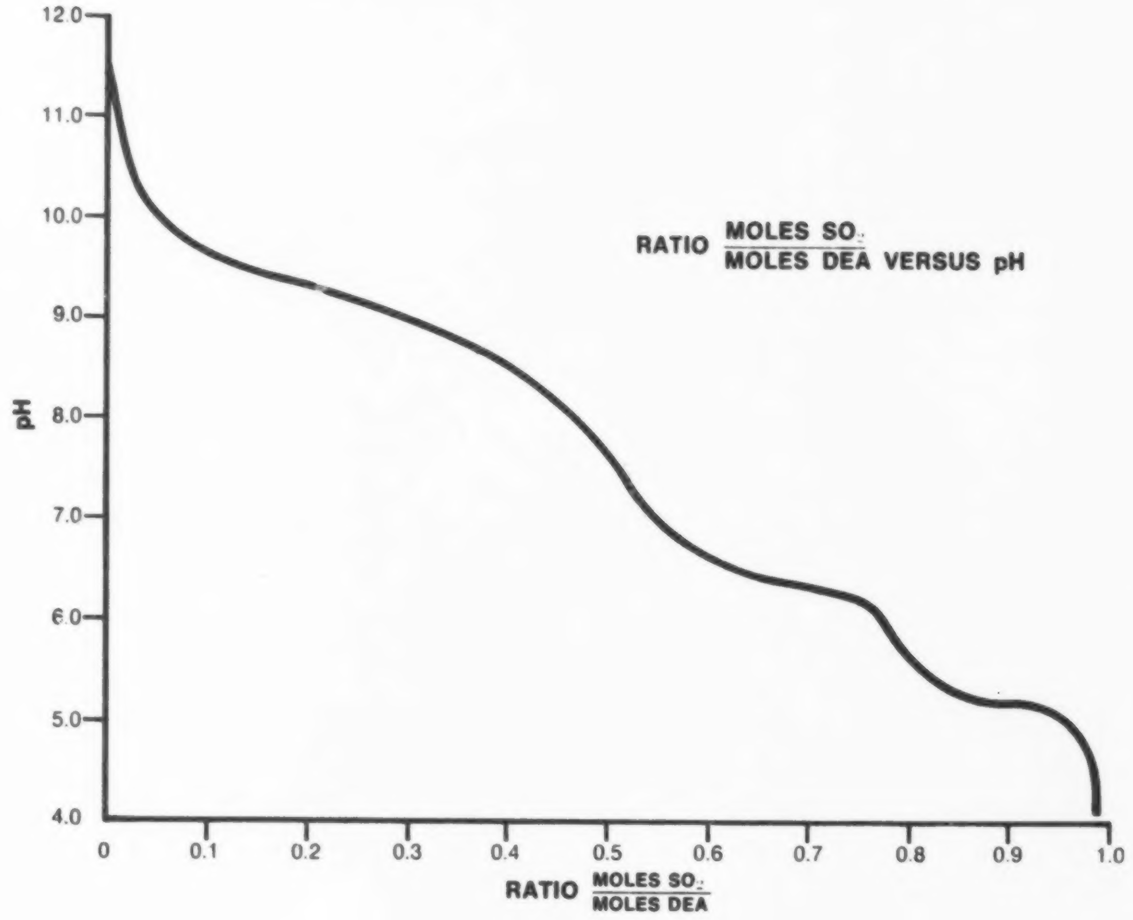


FIGURE 2

CALSOX Process

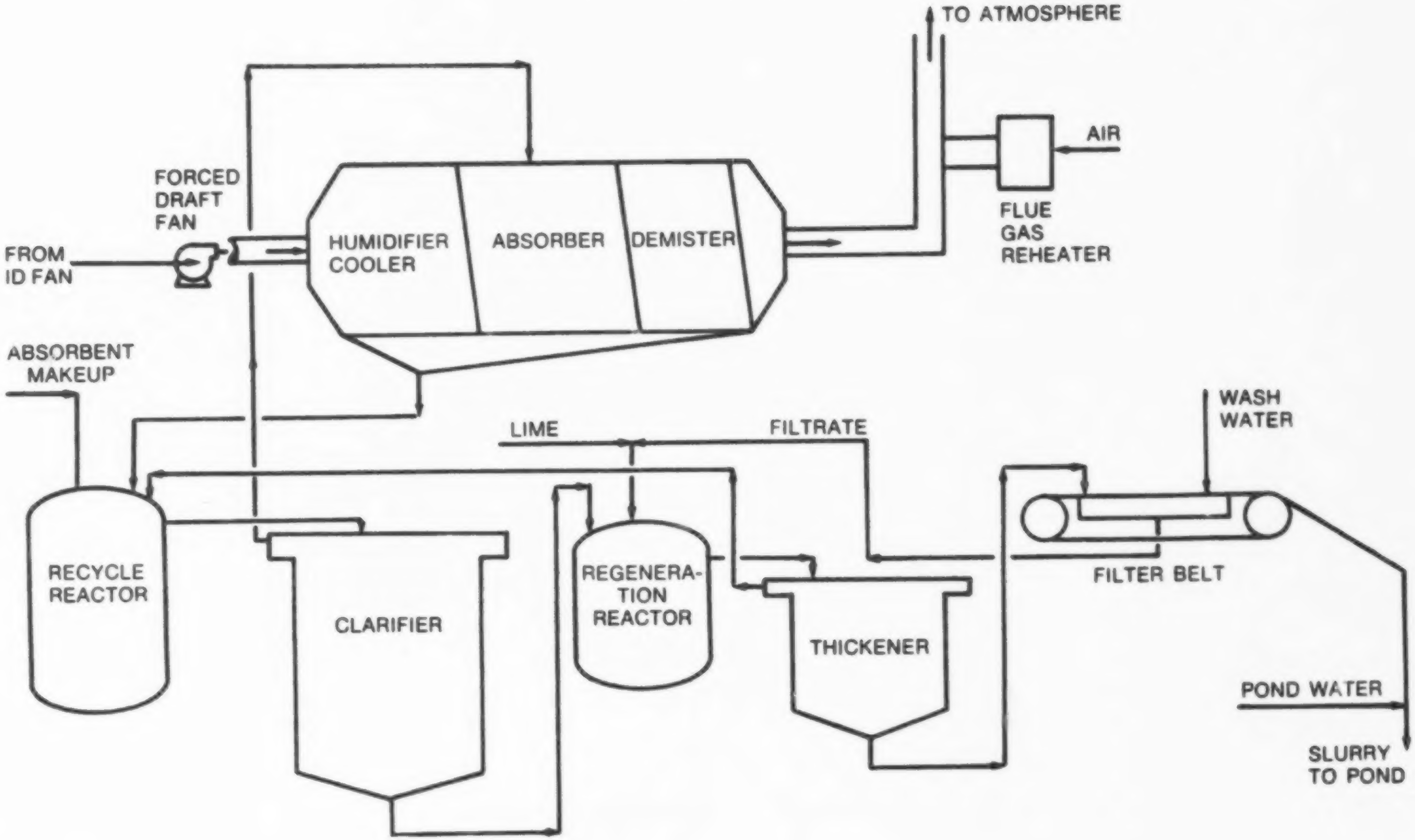

TO ATMOSPHERE
AIR
FLUE GAS REHEATER
FORCED DRAFT FAN
FROM ID FAN
HUMIDIFIER COOLER
ABSORBER
DEMISTER
ABSORBENT MAKEUP
LIME
FILTRATE
WASH WATER
RECYCLE REACTOR
CLARIFIER
REGENERA-TION REACTOR
THICKENER
FILTER BELT
POND WATER
SLURRY TO POND

FIGURE 3

CALSOX System Pilot Plant Flow Sheet

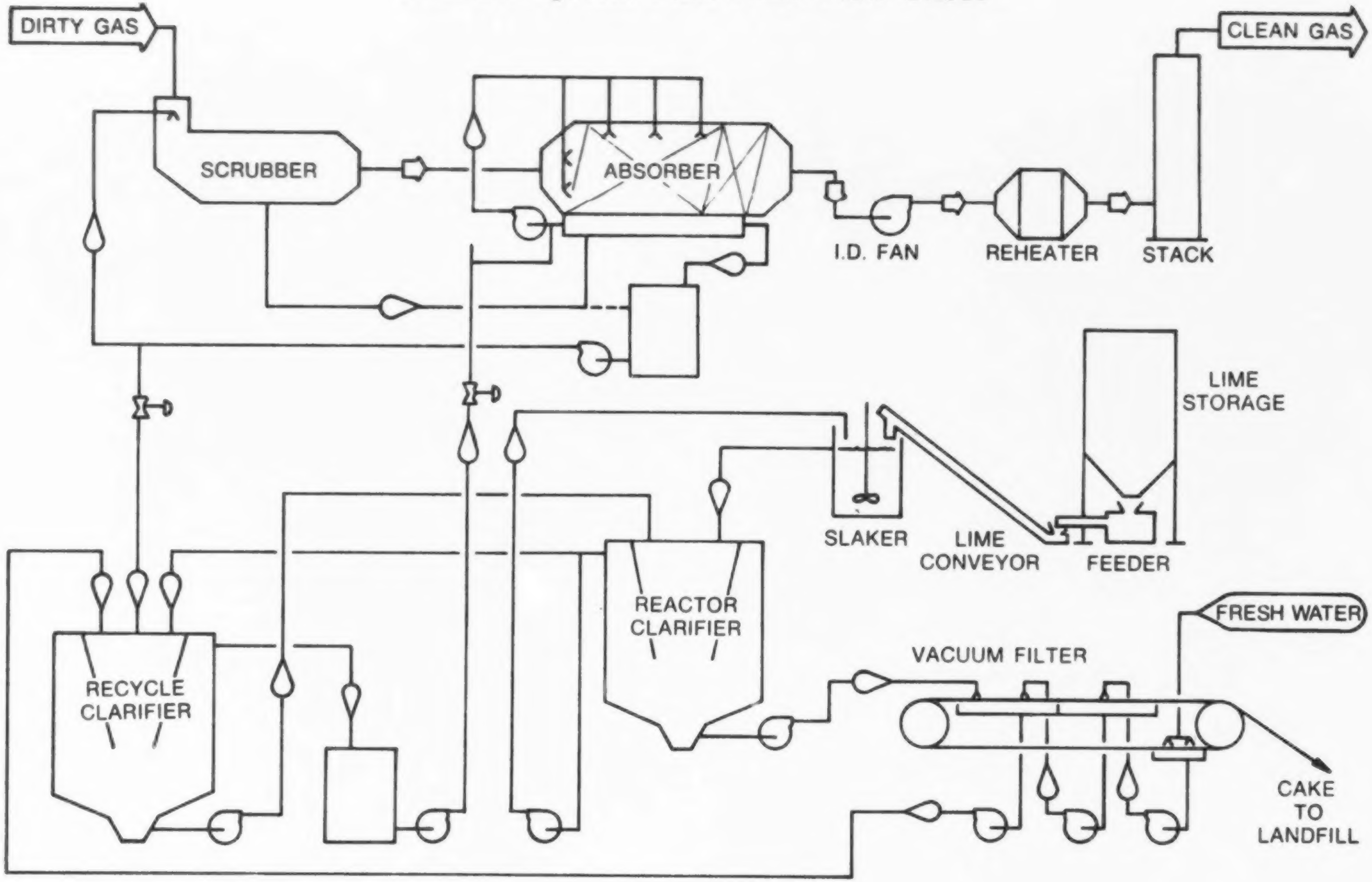
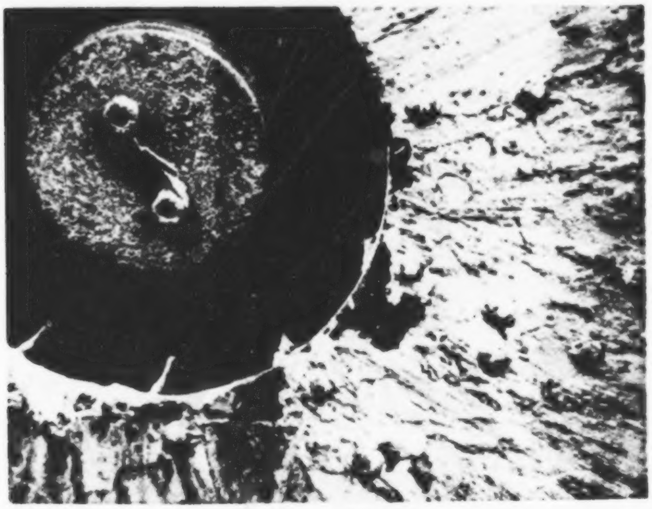
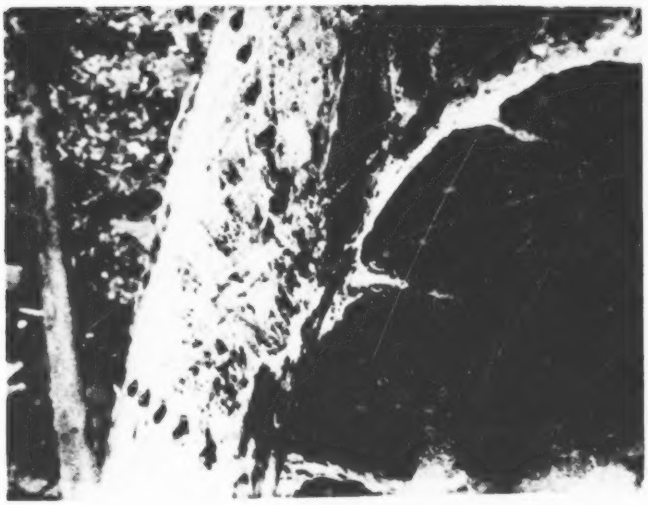

DIRTY GAS
SCRUBBER
ABSORBER
I.D. FAN
REHEATER
STACK
CLEAN GAS
LIME STORAGE
SLAKER
LIME CONVEYOR
FEEDER
REACTOR CLARIFIER
RECYCLE CLARIFIER
VACUUM FILTER
FRESH WATER
CAKE TO LANDFILL

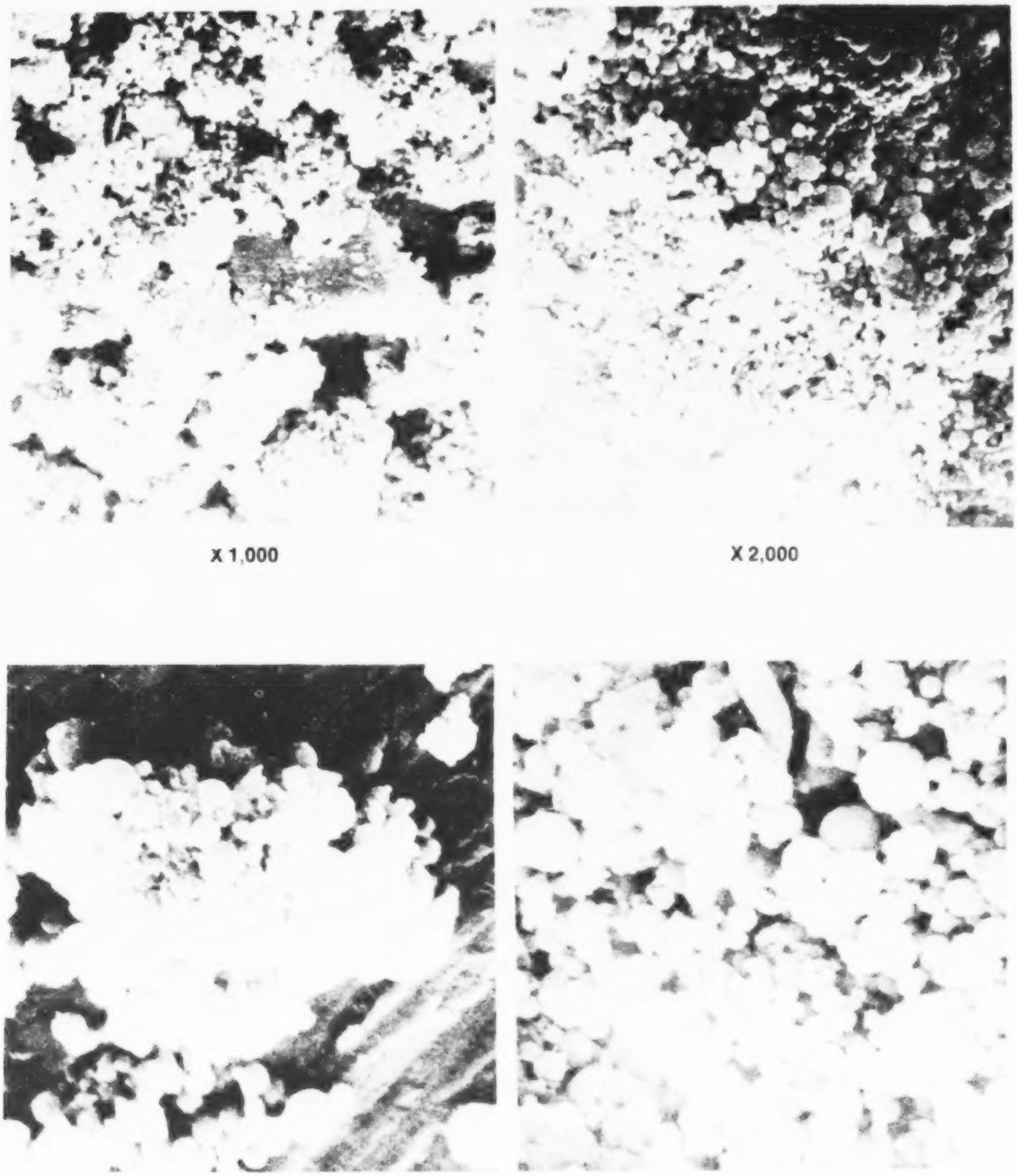
FIGURE 4



Inlet to Fan Wheel
Showing Hub and Front Flange



Between Radial Blades
Showing Edge of Blades and Front Flange



X 1,000

X 2,000

X 5,000

X 5,000

FIGURE 5

Deposits on Fan

FIGURE 6

Landfill Schematic at IPALCO

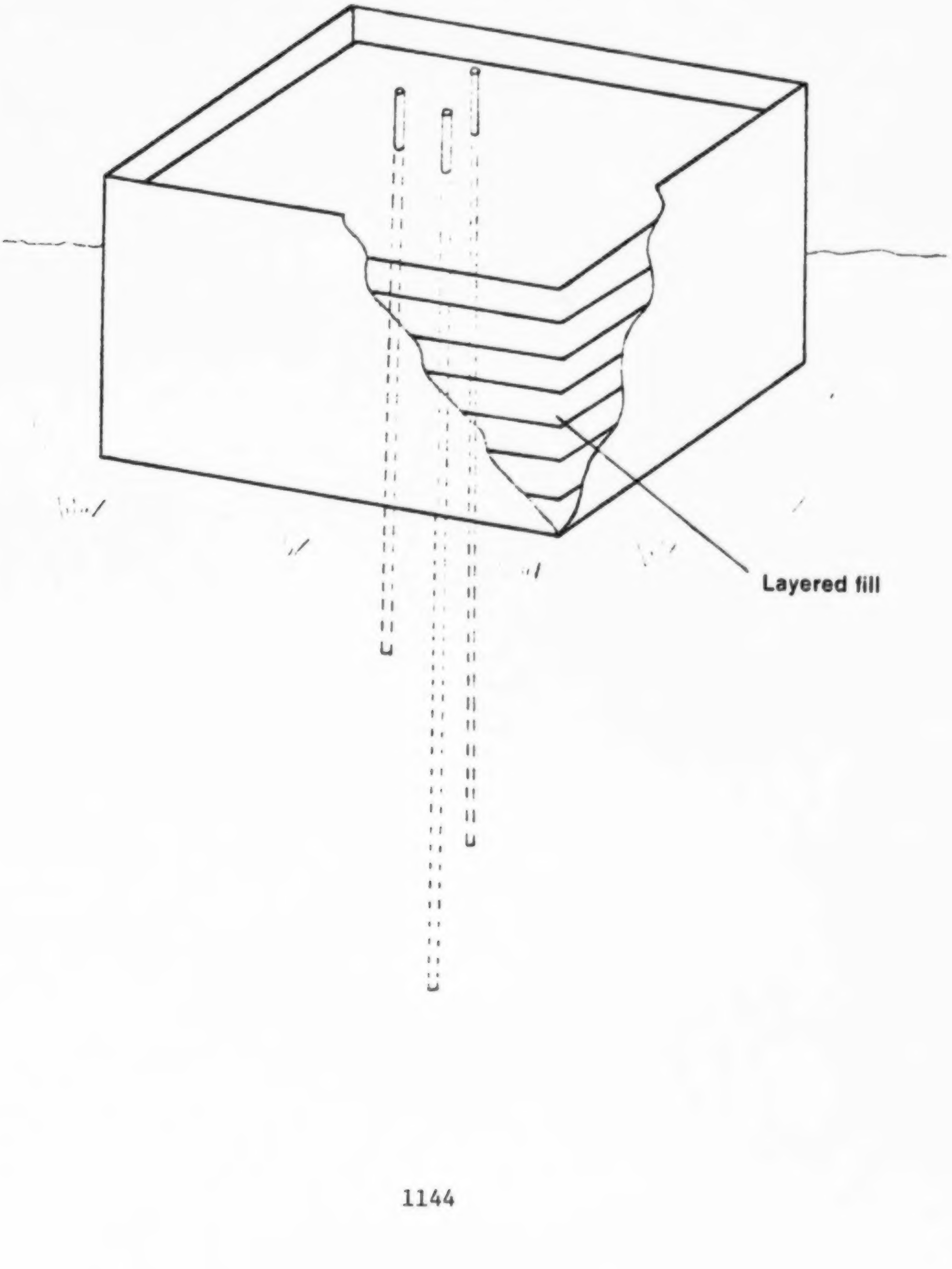
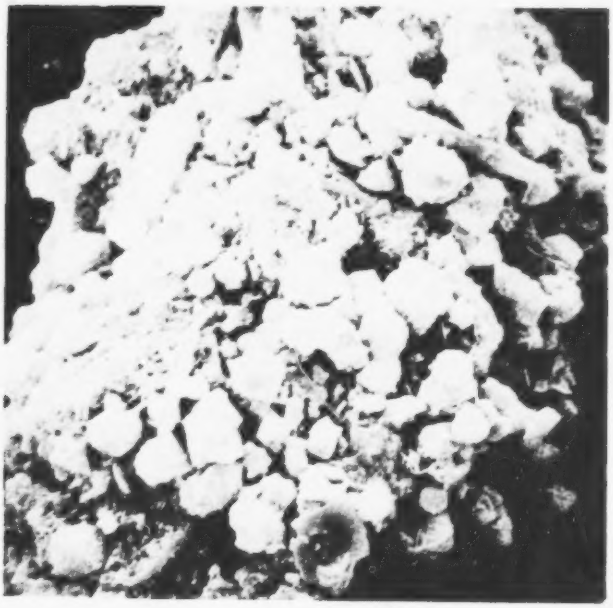

Layered fill

FIGURE 7

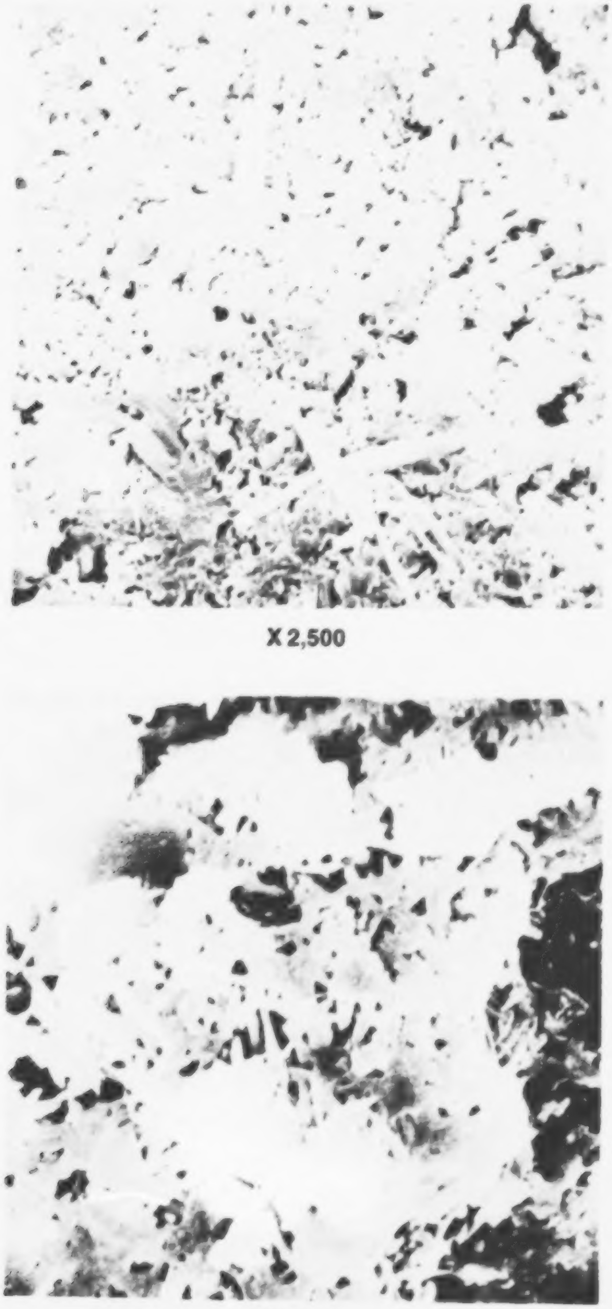
Photo Micrograph — Fresh Cake



X 1,800

FIGURE 8

Photo Micrograph — Aged Cake



X 2,500

X 5,000

FIGURE 9

CALSOX System Plot Plan IPALCO #7 Unit

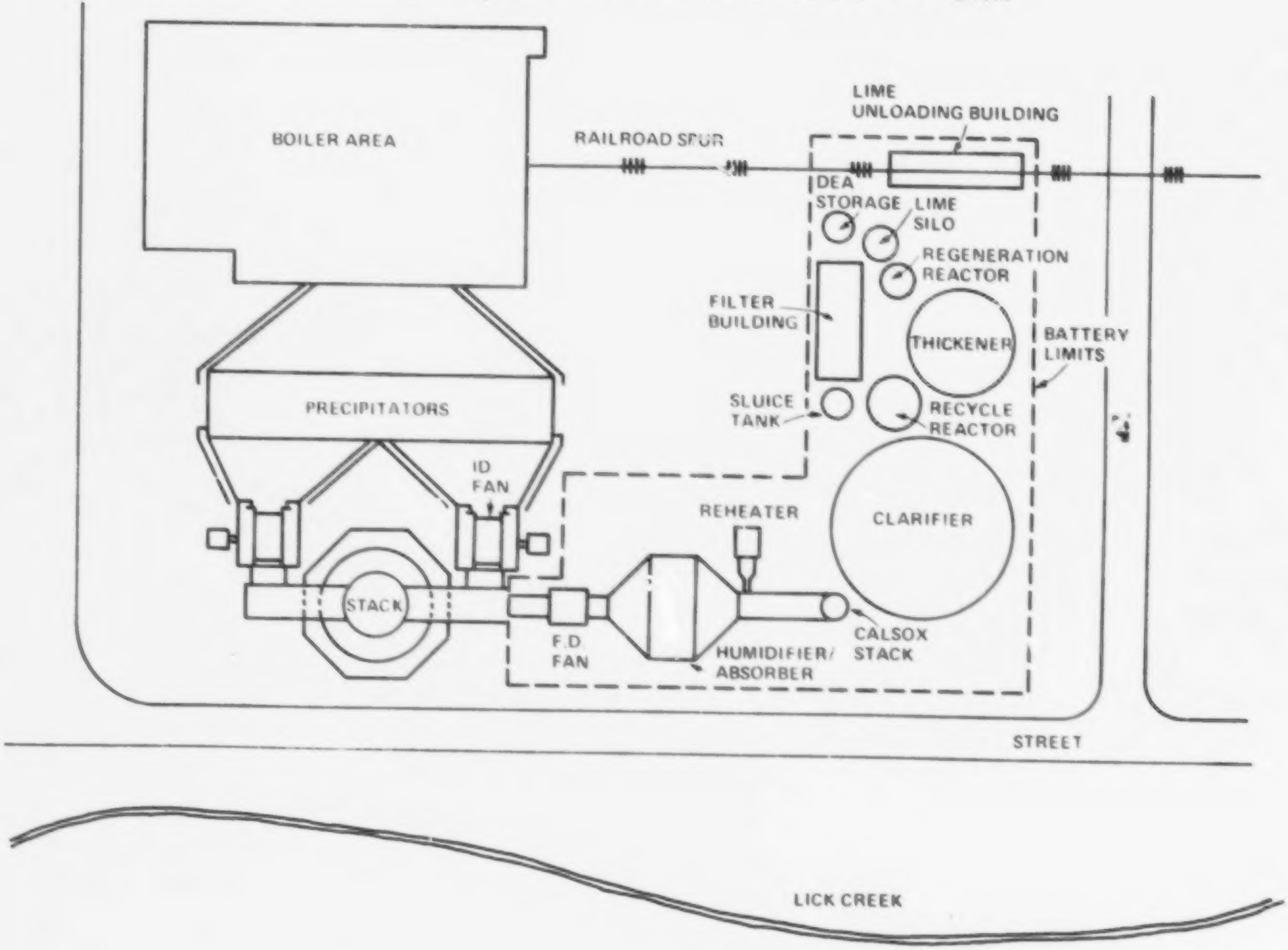

LIME UNLOADING BUILDING
BOILER AREA
RAILROAD SPUR
DEA STORAGE
LIME SILO
REGENERATION REACTOR
FILTER BUILDING
THICKENER
BATTERY LIMITS
PRECIPITATORS
SLUICE TANK
RECYCLE REACTOR
ID FAN
REHEATER
CLARIFIER
STACK
F.D. FAN
HUMIDIFIER/ ABSORBER
CALSOX STACK
STREET
LICK CREEK

FIGURE 10
Calsox Process
Estimated Operating Costs
(125 Mw — 3.2% Sulfur Coal; 90% SO_2 Removal)

	ANNUAL QUANTITY	UNIT COST—$	ANNUAL COST—$	Mills/kwhr.
DIRECT COSTS				
Delivered Raw Materials				
DEA	518,000 Lbs.	$.18/Lb.	93,240	.108
Quicklime	18,200 Tons	$26/Ton	473,200	.541
Subtotal Raw Materials			566,440	.648
CONVERSION COSTS				
Operating Labor	11,650 Man Hrs.	$8/Man Hr.	93,200	.107
Supervision	1,450 Man Hrs.	$10/Man Hr.	14,600	.017
Steam	218,750M Lbs.	$.50/M Lbs.	109,400	.125
Process Water	70,000M Gal.	$.1/M Gal.	7,000	.008
Electricity	18,900,000 kwhr.	$.0038/kwhr.	72,000	.082
Instrument Air	26,300M Ft³	$.15/M Ft³	4,000	.004
Maintenance, Labor & Materials	.04 x $6,000,000 — (Fixed Investment)		240,000	.274
Laboratory			20,000	.022
Subtotal Conversion Costs			560,200	.639
INDIRECT COSTS				
Average Capital Charges at 15% of Total Capital Invested			1,350,000	1.543
Overhead				
Plant, 20% of Conversion Costs			112,000	.128
Administrative, 10% of Operating Labor			9,300	.011
Subtotal Indirect Costs			1,471,300	1.682
TOTAL OPERATING COST			2,597,940	2.969

BASIS:
Remaining Power Plant Life — 30 Years
Stack Gas Reheat to 170°F
Power Plant On-Stream 7,000 Hr./Year
Capital Investment $9,000,000

ACKNOWLEDGEMENTS:

1 Proprietary term and trademark of Monsanto Enviro-Chem Systems, Inc.
2 Trademark of Riley Company.
3 Trademark of Robbins and Myers, Inc.

WESTVACO ACTIVATED CARBON PROCESS FOR SO_x RECOVERY AS ELEMENTAL SULFUR

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G. N. Brown
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S. L. Torrence

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Research Center
North Charleston, South Carolina

Abstract

An all dry, fluidized bed process using activated carbon for the effective recovery of SO_2 as elemental sulfur from stack gas has been demonstrated in a 20,000 cfh integral pilot plant. The granular carbon was continuously recycled over 20 times between a flue gas slipstream of an oil fired boiler for SO_2 removal and the sulfur recovery steps. The performance of the carbon remained at a high level over the 300 hour test with no undue chemical or mechanical loss of carbon. Over 90% of the 2,000 ppm sulfur oxides was removed from the flue gas as sulfuric acid by catalytic oxidation and subsequent hydrolysis within the carbon granule. In the first of two recovery steps, the acid loaded carbon was initially contacted at 300°F with internally produced hydrogen sulfide for conversion of the acid to elemental sulfur. The by-product sulfur was then thermally stripped from the carbon and the required H_2S produced by reacting the remaining sulfur on carbon with an external source of hydrogen at 1000°F.

Sufficient process and design information was developed from the data obtained in the integral run and prior stepwise pilot equipment operation to permit scale-up to a 15 MW prototype, the next anticipated development stage. The preliminary design includes installation on a coal fired boiler and the use of a coal fed gas producer to supply the necessary reducing gas. An economic assessment of a conceptual design for the SO_2 removal process as applied to a 1,000 MW coal fired boiler indicated capital and operating costs competitive to costs of other regenerable systems.

Much of this information was developed under a contract partially funded by the Environmental Protection Agency with Mr. Leon Stankus acting as project officer. However, EPA does not necessarily endorse the product or process.

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WESTVACO ACTIVATED CARBON PROCESS
FOR SO_x RECOVERY AS ELEMENTAL SULFUR

INTRODUCTION

Activated carbon as used in dry regenerable SO_2 processes avoids the critical control of chemical reactions necessary in wet processes and the costs and problems involved in separating water from by-product, either for recovery or disposal. Additionally, in the wet processes, flue gas reheating may be necessary for fan protection and plume control. Carbon processes which have or are being used all depend upon the catalytic and sorptive character of the carbon which is utilized for conversion of the SO_2 to sulfuric acid within the carbon granules. The processes generally differ in the mode of removal and recovery of the sulfuric acid from the carbon, i.e. either by thermal regeneration in which the acid reacts chemically with the carbon to produce a SO_2 rich by-product off-gas or by washing the acid loaded carbon with water to produce a weak sulfuric acid. Further differences exist in the additional methods of upgrading the by-product streams through add-on steps for conversion of the SO_2 gas stream to elemental sulfur or concentrated sulfuric acid. The method of flue gas-granular carbon contacting also varies in that fixed beds or moving beds with an upflow or crossflow gas pattern are used. Particle size and characteristics of the carbon granules with respect to the rate of SO_2 removal may differ, affecting pressure requirements and equipment size.

Westvaco, as a major producer of activated carbon, embarked on a program in which carbon, with a high SO_2 pickup rate capability, is recycled with regeneration of the carbon achieved by reducing the sulfuric acid chemically within the process to elemental sulfur without the carbon being consumed. These techniques would also have potential application to regeneration in any other processes which adsorb SO_2 as sulfuric acid. Furthermore, the fluidized bed was selected for gas-solid contacting in this development as one approach to permit handling relatively large volume rates of gases in contact with recirculating carbon solids. Other contacting methods may also have merit also but the effectiveness of fluidized carbon bed systems has already been demonstrated in large commercial units in existence[1], handling gas rates up to 540,000 cfm. The feasibility of using such a carbon system was confirmed in bench scale and small pilot equipment whereby H_2S in contact with the sulfuric acid on the carbon resulted in conversion to elemental sulfur which was then stripped off the carbon by heating. Part of the sulfur was reacted with an outside source of hydrogen to produce the needed H_2S.

The selection of a granular activated carbon and identifying the major variables in the process chemistry served as a basis for the joint work under an EPA contract which essentially involved scaling up the SO_2 removal sorption and the regeneration-sulfur recovery steps to a 20,000 cfh pilot plant. The objectives of the contract were to develop further information on each process step initially and to finally demonstrate the technical feasibility of the entire process and to evaluate the performance of the carbon under extended recycling conditions in an integrated pilot plant using flue gas from an oil fired boiler.

PROCESS CONCEPT

In the Westvaco Process dry granular activated carbon is contacted with flue gas at stack gas temperatures. The SO_2 is removed through catalyzed oxidation to SO_3 and a subsequent hydrolysis to sulfuric acid which remains sorbed in the carbon granules, i.e.

$$SO_2 + 1/2\ O_2 + H_2O \xrightarrow[\text{Carbon}]{\text{Activated}} H_2SO_4\ \text{(Sorbed)} \qquad (1)$$

Sufficient water vapor and oxygen are present normally in the flue gas for the reaction. This reaction takes place in a staged fluidized bed vessel with provisions for adjusting the temperature for optimum SO_2 removal rates.

The sulfuric acid loaded carbon is transported mechanically to a second fluidized bed reactor wherein the acid comes in contact with hydrogen sulfide to produce elemental sulfur, which remains in the carbon granules, and water vapor which is exhausted. Temperatures near 300°F are required for the reaction, i.e.

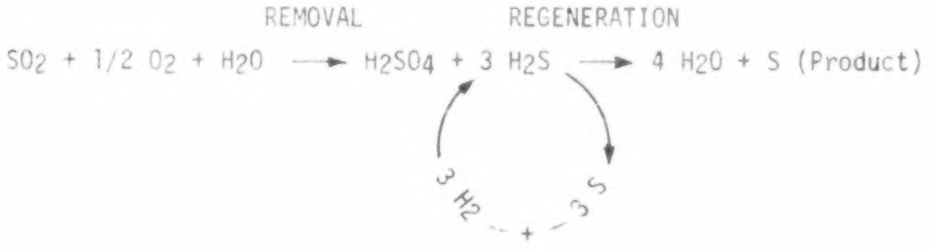
$$H_2SO_4 + 3\ H_2S \xrightarrow[\text{Carbon}]{\text{Activated}} 4\ S + 4\ H_2O \qquad (2)$$

Generation of the required hydrogen sulfide and the removal of the elemental sulfur for recovery is accomplished in a third fluidized bed reactor according to:

$$3\ H_2 + 4\ S \xrightarrow[\text{Carbon}]{\text{Activated}} 3\ H_2S + S\ \text{(Product)} \qquad (3)$$

The thermal stripping of the sulfur and the reaction to produce H_2S requires temperatures near 1000°F.

In essence the entire process chemistry could be depicted by the following in which the reductant hydrogen is attached to a recycled sulfur loop to become more reactive as intermediate product, H_2S, for reduction of the acid to sulfur and water vapor.



$$SO_2 + 1/2\ O_2 + H_2O \xrightarrow{\text{REMOVAL}} H_2SO_4 + 3\ H_2S \xrightarrow{\text{REGENERATION}} 4\ H_2O + S\ \text{(Product)} \qquad (4)$$

The hydrogen may be supplied through a number of commercially available gasifiers utilizing coal or other fossil fuels. Heating of the regenerating reactors may be provided by conventional fuel burning units.

The carbon serves as a vehicle for promoting the reactions efficiently but does not directly take part. It is recycled between the SO_2 removal vessel to the regeneration vessels where its activity is restored to the initial level.

The steps in this process concept were studied separately and finally in combination for a completely integrated demonstration in pilot plant equipment.

PILOT EQUIPMENT AND OPERATION

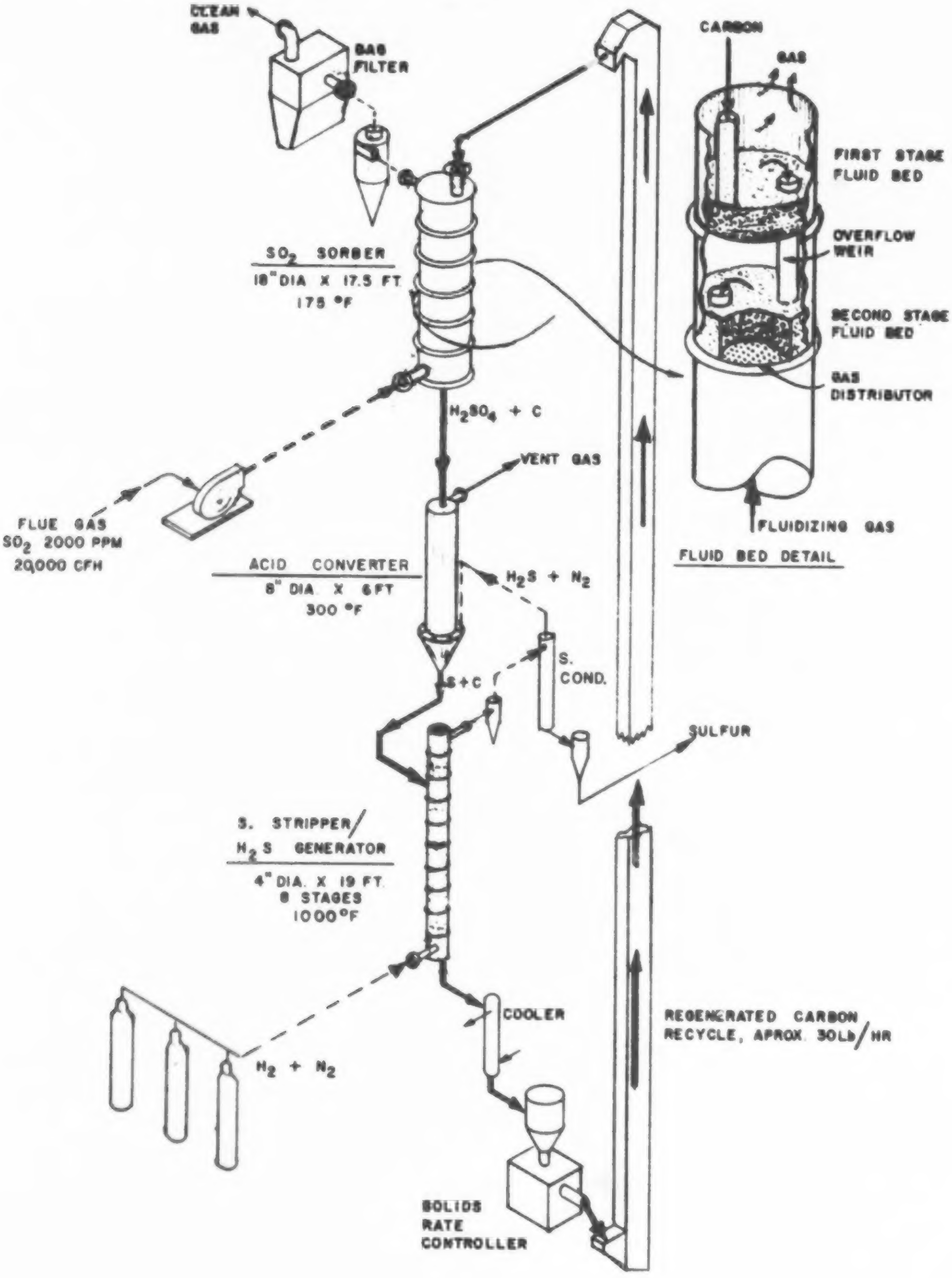
Integral Operation

The pilot plant evolved finally into three pieces of equipment, a sorber, an acid converter and a sulfur stripper/H_2S generator through which granular carbon flows by gravity as essentially shown in Figure 1. Reacting gases flow counter-current to the solids in each of the vessels at the appropriate temperatures and rates to carry out the necessary functions. Flue gas from an oil fired boiler is pumped through the SO_2 sorber at rates near 20,000 cfh at stack gas temperatures for removal of SO_2 and SO_3. The only other constituent introduced to the pilot plant is the gas stream containing cylinder hydrogen which is fed to the sulfur stripper/H_2S generator reactor for production of H_2S and stripping off of the by-product sulfur. The sulfur is ultimately removed from the system in molten form in the condenser. The sulfur-free gas containing H_2S then passes through the sulfur generator for reaction with the sulfuric acid on the carbon for conversion to elemental sulfur. The spent gas from the sulfur generator is vented.

Heating and cooling requirements for the gases and carbon during integral pilot operation are met with electrical resistance heating in the case of the acid converter and sulfur stripping/H_2S generator and direct water spray for cooling the SO_2 sorber. All are automatically adjusted except for the acid converter.

Recirculation of the carbon through the system is accomplished by gravity flow through the reaction vessels and raised for recycle mechanically by bucket elevator. The recirculating rate of the carbon, normally about 30 lbs./hr., is controlled automatically by a gravimetric solids rate feeder. For material balance purposes, any dust in the major streams is collected through cyclones and bag filters.

FIGURE I. WESTVACO PROCESS INTEGRAL PILOT PLANT


CLEAN GAS
BAG FILTER
SO_2 SORBER
18" DIA X 17.5 FT
175 °F
H_2SO_4 + C
VENT GAS
FLUE GAS
SO_2 2000 PPM
20,000 CFH
ACID CONVERTER
8" DIA. X 6 FT
300 °F
H_2S + N_2
S + C
S. COND.
SULFUR
S. STRIPPER/
H_2S GENERATOR
4" DIA. X 19 FT.
8 STAGES
1000°F
H_2 + N_2
COOLER
SOLIDS
RATE
CONTROLLER
REGENERATED CARBON
RECYCLE, APROX. 30 Lb/HR
CARBON
GAS
FIRST STAGE
FLUID BED
OVERFLOW
WEIR
SECOND STAGE
FLUID BED
GAS
DISTRIBUTOR
FLUIDIZING GAS
FLUID BED DETAIL

Main Reactors - Description

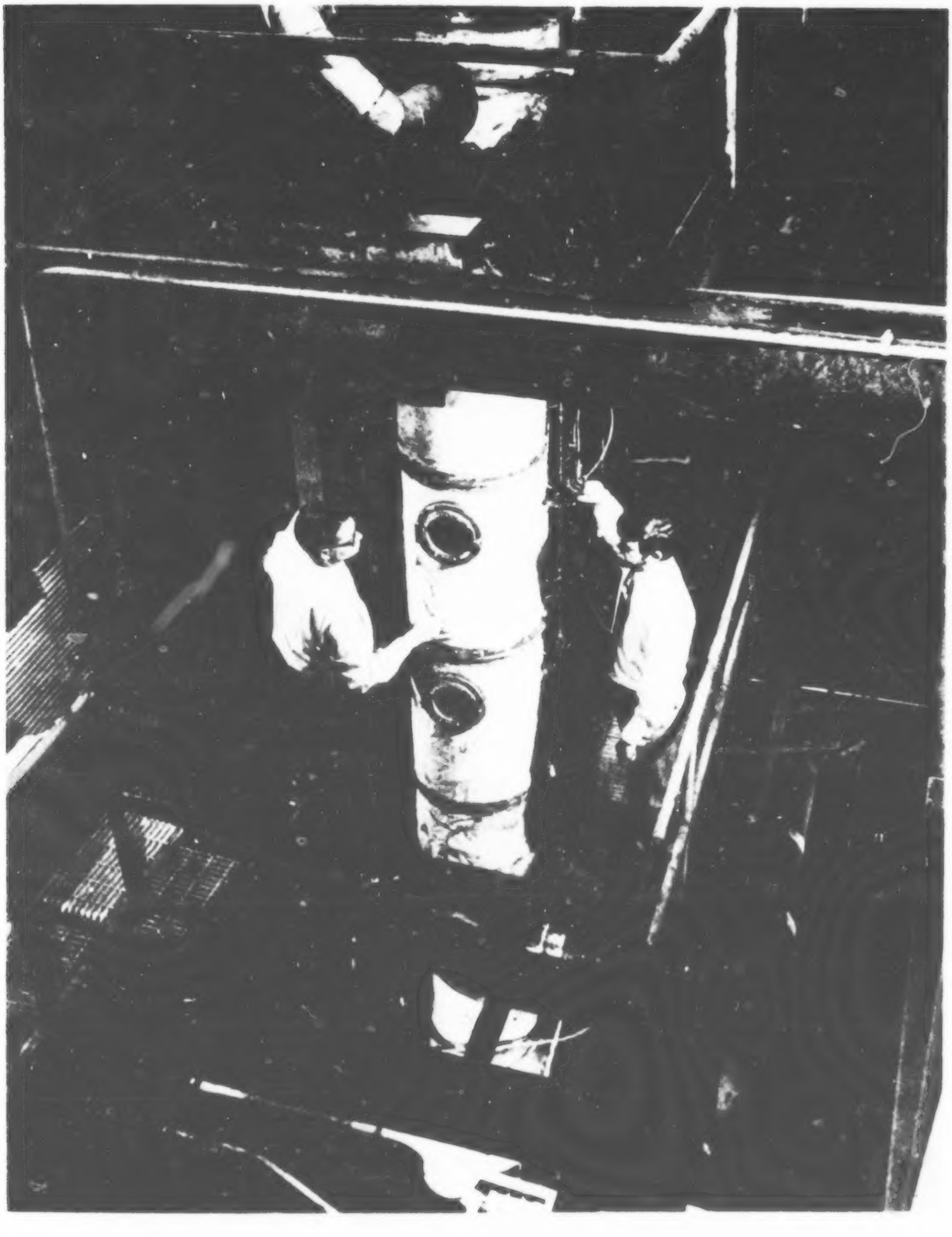
SO_2 Sorber

The sorber consists of an 18 inch diameter x 17.5 ft. high vessel with 5 fluidized beds of carbon, each bed having an expanded bed depth of 12 inches of carbon with the exception of the bottom bed which has 8 inches. The carbon is fed at a controlled rate to the top stage and flows by gravity through the overflow weirs/downcomers from stage to stage through the column. A uniform gas velocity across each stage of the reactor is maintained through a perforated gas distributor plate, as shown in the cutaway detail in Figure 1. Flue gas containing $\sim$2,000 ppm SO_2 flows upward at a rate of 20,000 cfh. The inlet flue gas temperature is at stack gas conditions of near 300°F which is the temperature maintained in the bottom fluid bed stage where the SO_3 is removed. The bed temperatures of the next stage are decreased to the desired level, 175°F, through a water spray injected directly into a carbon bed. Temperatures of the upper carbon bed stage are allowed to seek their own level. Figure 2 is a photograph of the actual reactor installation.

Acid Converter

In the integral pilot runs the acid converter consisted of a moving bed unit 8 inches in diameter containing a carbon bed depth of about 6 feet. Plug flow of solids through the reactor was assured through a specially designed cone bottom section and particle residence time testing prior to use. Temperature control in the range of 300°F was effected by external electrical heating of the reactor walls and by adjusting the moisture content of the acid loaded carbon feed. The H_2S containing gas enters the bottom of the reactor through a distributing zone for countercurrent contact with the carbon flowing downward. The H_2S depleted off-gas was vented from the top of the reactor.

Figure 2. Continuous 18 inch diameter, 5 stage SO_2 and SO_3 adsorber operating on flue gas from a 50 MW oil fired boiler.



Early in the program, studies showed that sulfur generation could be acceptably performed in staged fluidized beds. However, the reactor size needed for accommodating the gas and carbon flows of the integral pilot design was prohibitively small, about 2 inches in diameter, to be practically operated. A moving bed reactor was designed for the integral pilot plant using preliminary information developed on a bench scale.

Sulfur Stripper/H_2S Generator

Removal of the by-product sulfur and reaction of the hydrogen with the remaining sulfur on the carbon is performed in a 4 inch diameter, 8 stage fluidized bed reactor. The carbon loaded with sulfur is fed to the third stage from the top and flows downward through overflow weirs maintaining bed heights of five inches. Batch carbon beds are maintained in the upper two beds to promote the conversion of sulfur to H_2S. Hydrogen containing gas is fed to the reactor bottom at rates near 220 scfh while reactor temperatures near 1000°F were maintained with external electrical heaters. The off-gas containing vaporized sulfur and H_2S is passed through a dust removing cyclone and then the sulfur condenser before use in the acid converter. Regenerated carbon discharging from the reactor was cooled in an indirect heat exchanger for recycling back to the SO_2 sorber by bucket elevator.

Process Unit Operations

In developing the design and operating information needed for the integral pilot plant each of the process steps was studied separately in the described main reactors and in other equipment. Two smaller fluid bed SO_2 sorbers, one of a 6 inch diameter and one of a 4 inch diameter, in addition to a thermogravimetric analyzer were used prior to testing of the 18 inch diameter reactor. Batch pilot and bench scale equipment was used for initial study of the sulfur generation and sulfur stripping/H_2S generation steps. This information was used for developing rate equations for the reactors and conditions involved.

Fluidization Mechanics

Some interrelation exists between the conditions for maintaining the process chemistry and fluidization requirement in operating the fluid bed reactor. Information was developed in room temperature mock-up equipment of pilot plant size prior to the integral run on fluidization, including required gas velocities, pressure drop, gas distributor design, entrainment, and dust generation.

Instrumentation and Control

Sufficient instrumentation is available to maintain the desired operating conditions during steady state conditions and to collect the data necessary for performance evaluation. All input gas flow rates are monitored through meters and checked by gas analysis instruments. Temperatures and pressures at appropriate points within the system and reactors are either indicated or recorded. The control and instrument panel for the pilot plant is shown in Figure 3.

Sample Points and Analysis

Ports were positioned on the inlet and outlet of each of the three reactors for sampling the granular carbon to determine the amount and form of sulfur and moisture content. Gas sample ports were also positioned so that various inlet and outlet points in the system were analyzed chromatographically for H_2, O_2, H_2S, SO_2, N_2, CO_2, CO and H_2O at the desired time. Samples of the solid were analyzed using standard tests for measuring the physical and adsorption properties.

Granular Carbon

The carbon used in the integral pilot operation is a commercially producible coal based carbon with a nominal 12x40 mesh size. The bulk density of the carbon was about 40 lbs./cu. ft. and the SO_2 removal properties and attrition resistance were 60 minimum and 97 maximum, respectively, as determined by specially designed tests. Although this is an improved carbon with respect to attrition resistance and is satisfactory for pilot testing, other carbons are being developed having superior properties for commercial use.

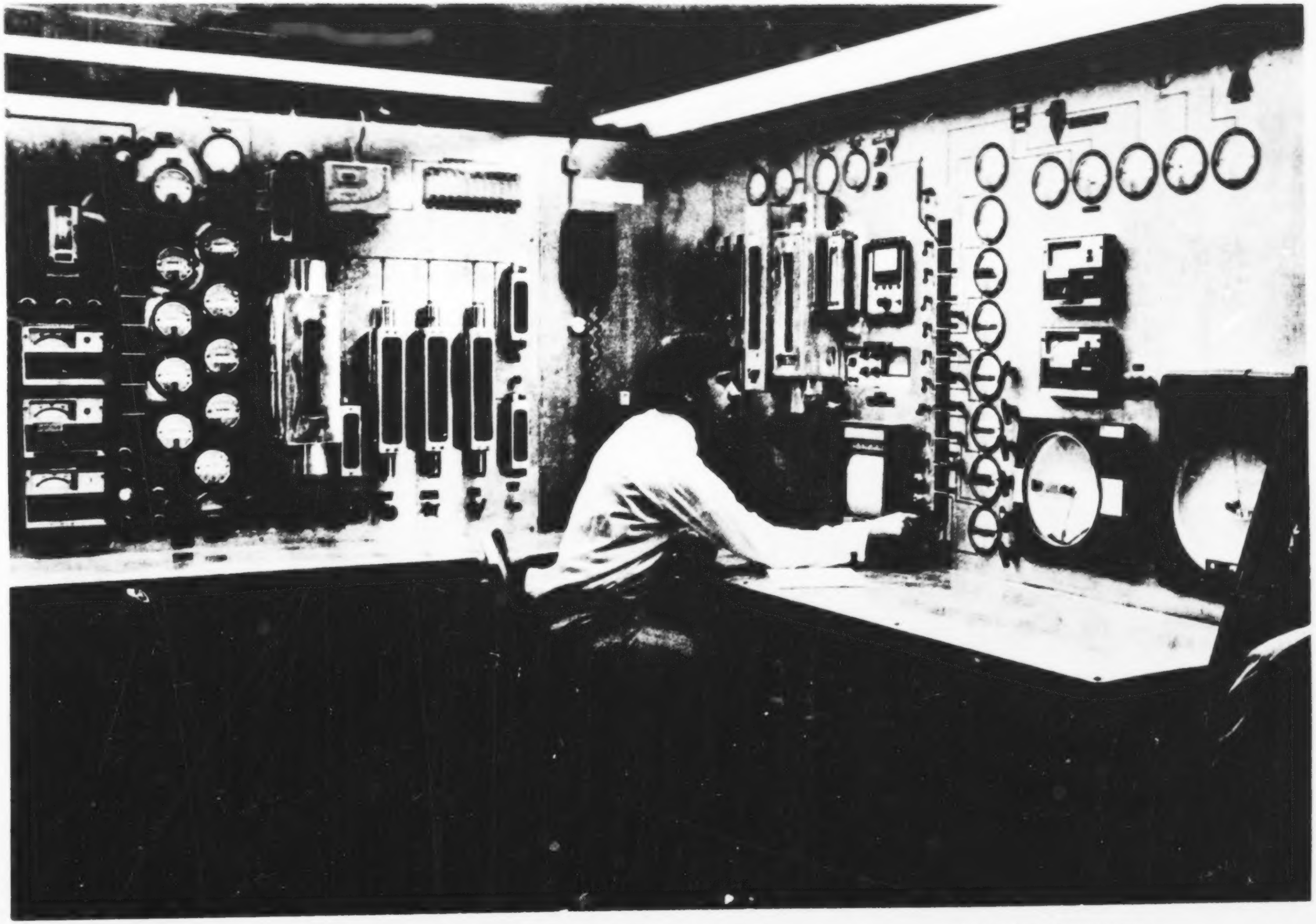


Figure 3. Control panel for integral pilot plant operating on oil fired boiler.

Flue Gas Characteristics

Gas used in the integral testing was flue gas from the stack of a 50 MW oil fired boiler having a mechanical dust collector. The sulfur content of the oil was about 1.8 - 2.0% S which produces about 1100 ppm SO_2 in the flue gas. In order to avoid variability at this stage of operation, provisions were made for injecting additional SO_2 into the flue gas to maintain a uniform level of SO_2 to the pilot plant. The temperature of the flue gas was kept at a stack gas temperature level of 300°F before introducing into the SO_2 sorber.

Reducing Gas Composition

The reducing gas was a mixture of hydrogen and nitrogen from gas cylinders. Hydrogen input rates were varied from 40 to 48% of the total flow to establish process requirements.

General Operating Procedure

In starting up the integral system a known quantity of carbon to be tested, about 500 pounds, was placed in the system to be recirculated while preheating with a start-up heater to approach the desired operating temperatures. The switch to flue gas was then made and the temperatures, carbon flow rate and gas flows, and compositions were adjusted to the estimated conditions needed. Manual adjustments were made to the SO_2 added to the flue gas above the actual oil produced SO_2 to maintain a constant level. The amount of carbon placed in the system was sufficient to minimize adding fresh carbon during the integral run and represents about 40% above that needed to fil the reactors and conveying system.

Selection of Conditions for the Integral Run

The general intent of the integral run was to maintain constant conditions over an extended period in which the granular carbon would be exposed to repeated sorption and regeneration conditions with H_2S produced in the process. Up to this time carbon had been exposed to flue gas during sorption but in the acid converter step only cylinder H_2S had been used. An arbitrary time of 30 cycles was initially selected for the integral run during which time any trend would be detectable and indicative of longer term effects. In addition, a 90% SO_2 removal efficiency was to be maintained with a sulfuric acid loading on the carbon of at least 18 lbs. acid/100 lbs. carbon. Other limits on acid conversion, sulfur recovery and operating conditions were selected based on pre-integral pilot and bench scale test results.

RESULTS AND DISCUSSION

Integral Pilot Plant Run

Overall Operation

A single batch of carbon was exposed to 21 sorption-regeneration cycles for steady state periods over a 300 hour operating time. Uniform conditions were maintained during this time for the SO_2 sorption operation; however, changes in hydrogen input to establish process requirements led to 3 steady state periods for regeneration. During this time the carbon was regenerated to its original activity in all cases. One major interruption was experienced in carbon handling which caused shutdown of the pilot plant, but care was taken in removing and replenishing the carbon from the equipment to assure minimum process disturbance.

Run Conditions

The run conditions in Table 1 were predetermined to meet the target goal of 90% SO_2 removal with an acid loading of at least 18 lbs. acid/100 lbs. carbon. The inlet flue gas was controlled at the rate of 22,000 acfh to the SO_2 sorber. The SO_2 content was adjusted as necessary to maintain 1900 to 2000 ppm and the inlet temperature was maintained at 300°F on the first stage of SO_3 removal with the next stage cooled by water spray to 175°F for SO_2 removal. The temperatures of the remaining stages were not controlled and were allowed to rise due to heat of reaction during SO_2 removal. Carbon bed depths of 3.5 inches on

TABLE 1. Range of operating conditions for integral pilot plant run.

	CONDITION
INLET FLUE GAS	
Gas Rate:	22,000 SCFH
Temperature:	300°F
Composition, SO_2:	1900-2000 PPM
SO_3:	50 PPM
NO:	150 PPM
O_2:	4.5 Vol. %
H_2O:	13 Vol. %
Inert Gas (CO_2, N_2):	Balance
SO_2 SORBER	
Temperature, Stage 1 (Bottom):	300°F
Stage 2 (H_2O Spray):	175°F
Carbon Bed Depth (Expanded):	Stage 1 - 8" Stages 2 to 5 - 12"
Fluidizing Velocity:	3.5 Ft./Sec. @ 300°F
Space Velocity:	3400 SCF Gas/CF Carbon-Hr.
REGENERATORS	
Acid Converter	
Temperature:	290°F (Avg.)
H_2S Inlet Rate:	Output from H_2S Gen. Range = 2.5-2.9 mol/moles
Space Velocity:	100 SCF Gas/CF Carbon-Hr.
S Stripper/H_2S Generator	
Temperature:	1000-1100°F
H_2 Inlet Rate:	3.4, 3.9, 4.3 moles H_2/mole SO_2 Sorbed
Space Velocity, Stripper:	2000-3100 SCF Gas/CF Carbon-Hr.
H_2S Generator:	6200-9300 SCF Gas/CF Carbon-Hr.
Fluidizing Gas Velocity:	1.8 - 2.7 Ft./Sec. @ 1000°F
CARBON RECYCLE RATE:	29 - 30 Lbs. C/Hr.

the bottom stage and 6 inches on each of the remaining stages were set for a total of 56 inches in an expanded state.

The recycle rate of carbon was set to achieve the desired acid loading based on the previous relationships developed between the operating parameters in the sorber.

Temperature and space velocity conditions for the acid converter and sulfur stripper/H_2S generator were selected based on earlier process unit test results. The amount of hydrogen flow to the generator was varied above the stoichiometric requirement of 3 moles/mole of SO_2 sorbed on the carbon. The amount of H_2S entering the sulfur generator was predetermined by the hydrogen input with no attempt to control this rate.

The pilot plant was started and operated over the extended period under the above conditions using the previously described procedures.

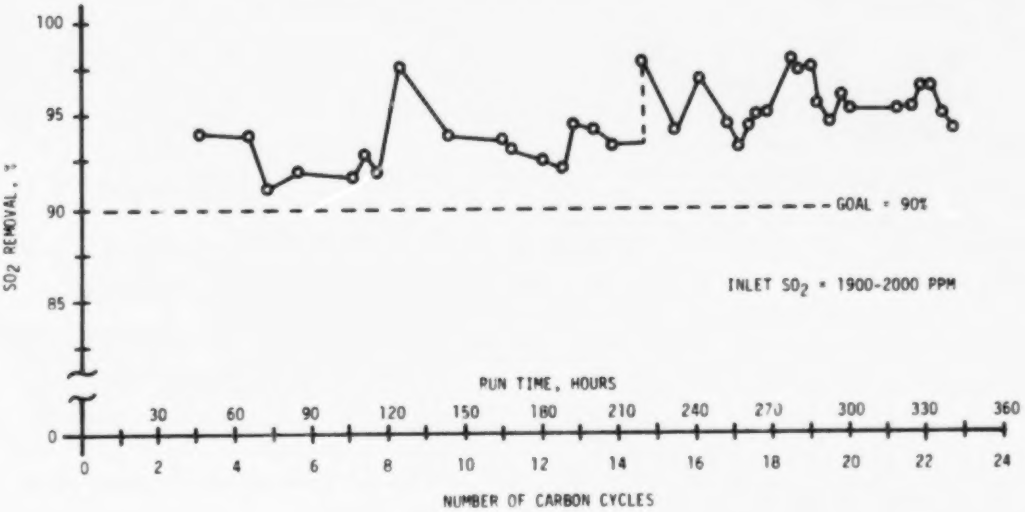
Overall Process Performance

The main factors observed in the pilot operation were the level of SO_2 removal during cycling of the carbon, the effects of hydrogen supplied to the system for reduction in terms of stoichiometric requirement, and the conversion of SO_2 pickup to elemental sulfur. Other factors were the detection of any carbon loss by chemical and/or mechanical means and the disposition of any excess hydrogen.

SO_2 Removal

The removal of SO_2 during the integral run over the 300 hour period is given in Figure 4. The flue gas, containing 1900 to 2000 ppm SO_2, was desulfurized to well above 90% with a maximum of 97% or corresponding to 60 ppm remaining in the effluent gas. By inspection of the plot, there does not appear to be any reduction in removal efficiency of the carbon. This has also been substantiated by analysis of the recycled carbon in laboratory tests. During the integral run the carbon was cycled through the system some 21 times based on a calculated carbon

FIGURE 4. SO_2 removal efficiency during integral pilot tests.



residence time of 15 hours in the integral system. The amount of SO_2 picked up by the carbon in terms of sulfuric acid averaged 24 lbs./100 lbs. carbon, substantially above target.

No corrosion or dew point problems were noted in operation at 175°F since the 30 - 50 ppm gaseous SO_3 in the flue is adsorbed on the carbon. This removal of SO_3 with carbon was demonstrated in previous studies.

The 150 ppm NO in the flue gas is not directly affected by the carbon and as such remains in the flue gas. The initial effect of the NO is to suppress the SO_2 pickup. This effect appears up to a NO concentration of about 150 ppm but not beyond. This aspect is covered more fully in a later section.

Regeneration Results

In the integral runs the intent was to demonstrate that the carbon could be repeatedly regenerated for reuse and to maximize the amount of elemental sulfur produced within the limitations of the present pilot equipment. The only deliberate change in regeneration conditions was in the hydrogen input. Other conditions were pre-set based on prior work.

As discussed in the preceding section, the activated carbon retained its adsorptive capabilities throughout the run, attesting to the suitability of regeneration under all hydrogen input conditions.

Sulfur By-product

It is important that the sulfur by-product from the regeneration system be a salable commodity. The element sulfur recovered from the pilot tests had characteristics as shown below:

Properties of Sulfur Product

Sulfur	99.7%
Ash	380 ppm
Carbon	2500 ppm
Acidity	2 ppm
Chloride	<2 ppm

These properties, measured for Westvaco by a sulfur producer, classify the sulfur collected as a commercial grade.

The small amounts of carbon in the sulfur, a result of fines carry-over, from the regenerator gave the sulfur a greenish cast. It was demonstrated that these fines could be readily filtered to give a bright sulfur product of 99.9% purity.

During these integral tests as with prior work, there was limited temperature control in the moving bed acid converter. As a result of higher than desired temperatures, a part of the sorbed acid decomposed to SO_2 in the upper part of the unit and was not readily available for conversion to sulfur. Thus a maximum of 85% conversion of the sorbed acid to sulfur was obtained with this equipment. Prior testing had shown that with proper temperature control essentially 100% conversion to sulfur is possible and this should be readily attainable in larger equipment where fluid beds will be used.

Effect of Hydrogen Input

Three levels of hydrogen input were evaluated during the integral runs and analysis on all the process streams were used in preparing the material balance presented in Table 2.

Table 2. Effect of hydrogen input on by-product recovery.

	Condition		
	A	B	C
TOTAL HYDROGEN INPUT (moles/mole available acid)	4.6	4.3	3.9
HYDROGEN USAGE (moles/mole available acid)			
1. Formation of by-product sulfur	2.90	2.88	3.0
2. Reaction with by-product sulfur to form H_2S	0.25	0.11	0
3. Reaction with chemisorbed oxygen to form H_2O	0.90	1.0	0.9
TOTAL MEASURED H_2 OUTPUT	4.05	3.99	3.90

Condition C essentially represents the process hydrogen input necessary for conversion of the available acid to elemental sulfur product. The hydrogen input above the stoichiometric ratio of 3 reacted with chemisorbed oxygen to form water and H_2S did not appear in the sulfur generator vent gas. The reaction of a part of the inlet hydrogen with chemisorbed oxygen had been observed in previous work and is apparently instrumental in retaining the activated carbon's activity upon cycling. As the hydrogen was increased from 4.3 to 4.6 a part of the product sulfur reacted to form H_2S which appeared in the vent gas, while formation of water essentially remained constant. The difference between the measured hydrogen input and output amounts to about 12% and could be the result of analysis error or, possibly, chemisorption of these small amounts of hydrogen on the carbon itself.

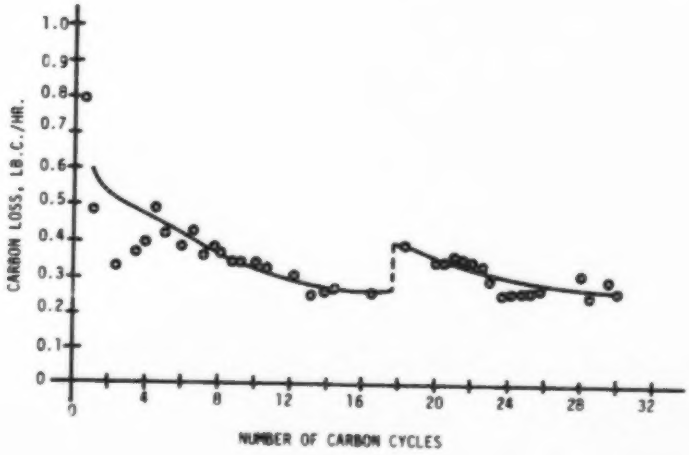
If the hydrogen ratio were lowered below those of Condition C, SO_2 formation would be expected at the expense of part of the product sulfur product. This would be the desired direction if the process is slightly out of balance since SO_2 can be readily recycled to the sorber.

The gas residence time in the regenerators is only about 15 seconds; therefore, response of the system to hydrogen input is very rapid. Thus, control should be readily achieved by monitoring regeneration off-gases and adjusting the hydrogen input.

Carbon Attrition

The activated carbon used in integral tests was improved compared to normal plant materials. The attrition rate measured with this material, Figure 5, showed an initial decrease, probably due to a

FIGURE 5. Activated carbon attrition rate during integral pilot tests.



rounding off of rough edges and then a stabilization at a rate of 0.26 lbs./hr. The data indicated nearly all of this attrition occurred in the fluidized beds of the SO_2 sorber. Additional work has shown that the combination of larger particle sizes and carbons with improved hardness will reduce the attrition rates to about 10% of the values measured here. These improvements will be incorporated in future scale-up work.

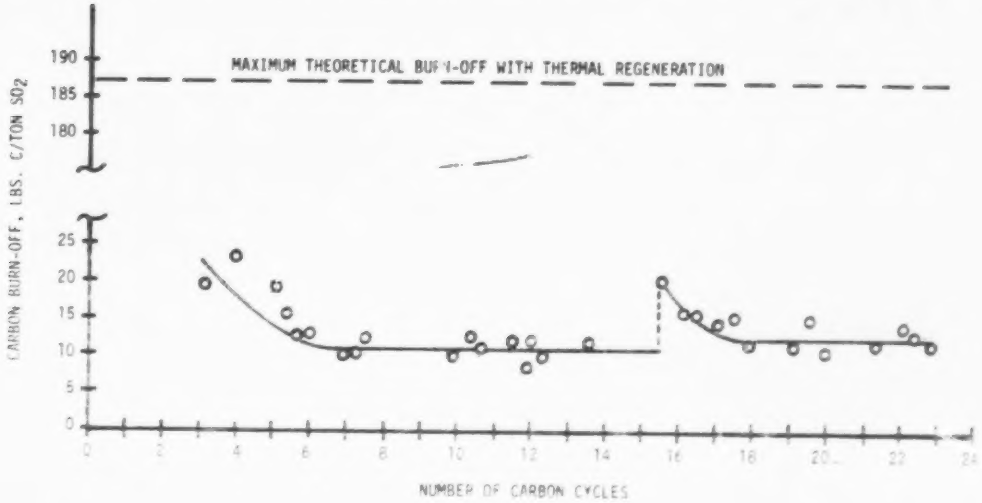
It is significant that there is no apparent increase in the attrition rate as the carbon was recycled thermally and chemically as has been observed with other solid adsorbents. The nature of SO_2 recovery with carbon, that it only provides a surface for catalysis and adsorption rather than actually chemically participating in the reactions as is done with metal oxides, probably results in the maintenance of structural integrity and strength of the carbon.

Carbon Burn-off

In passing through the regeneration sequence the activated carbon is exposed to temperatures progressively increasing from 300°F to 1000°F. To prevent chemical consumption at 1000°F in the regeneration sequence the sulfuric acid is reduced to elemental sulfur at 300°F. In addition to production of elemental sulfur, a goal of the Westvaco Process is to minimize the amount of carbon reaction to produce CO_2. Measurements were made on the CO_2 content of the regeneration off-gases to estimate the amount of "burn-off" that could be occurring in the process.

As shown in Figure 6, the carbon burn-off as calculated from CO_2 evolution reached a stable value of about 10 - 12 lbs. per ton of SO_2 sorbed from the flue gas. As shown by the dotted line this compares to a "burn-off" of 187 lbs. /ton if the carbon were consumed by reacting with all the sorbed acid under thermal regeneration conditions. This

FIGURE 6. Carbon burn-off during integral pilot tests.



reduction in burn-off of about 95% shows that the original objectives were achieved. By inspection of the data there was no apparent effect on burn-off when the hydrogen input was varied in the range of 3.9 - 4.6 moles/mole acid discussed earlier.

Complete conversion of the acid to sulfur was not required to prevent burn-off. Earlier experiments on the bench scale verified this fact, in that the addition of sulfur by various means considerably reduced the chemical consumption of the activated carbon during regeneration. This may have application in eliminating carbon burn-off in other carbon processes that produce SO_2 as a product or product intermediate.

As discussed earlier there was some thermal decomposition in the acid converter which would probably explain the small amount of burn-off measured.

If all of the CO_2 measured is a result of burn-off the low values measured here would correspond to a complete replacement of the inventory only about once every two years.

Effect of Variables and Design Relationships

Prior to the integral tests extensive variable studies were conducted on each process step to establish design relationships.

Considerable attention was given to the SO_2 sorber due to the potentially large variations in flue gas compositions and to the effect on the size of this reactor.

SO_2 Sorption

Bench scale tests of the effects of temperature, acid loading and SO_2, oxygen and water concentration on SO_2 removal are summarized in Figure 7. Nitric oxide, which is also normally present in flue gas, is not picked up on the carbon; however, it does affect the SO_2 sorption rate as shown in Figure 8. The effect of NO is constant above 100 ppm, well above that normally present in flue gas. A multiple regression analysis of all of the bench scale data resulted in a rate expression

FIGURE 7. SO_2 sorption rate model.

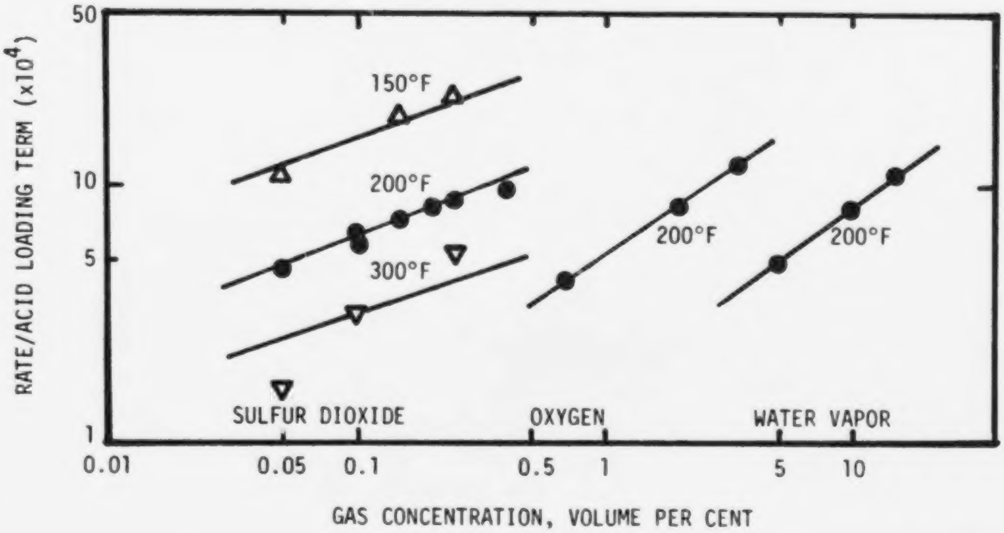
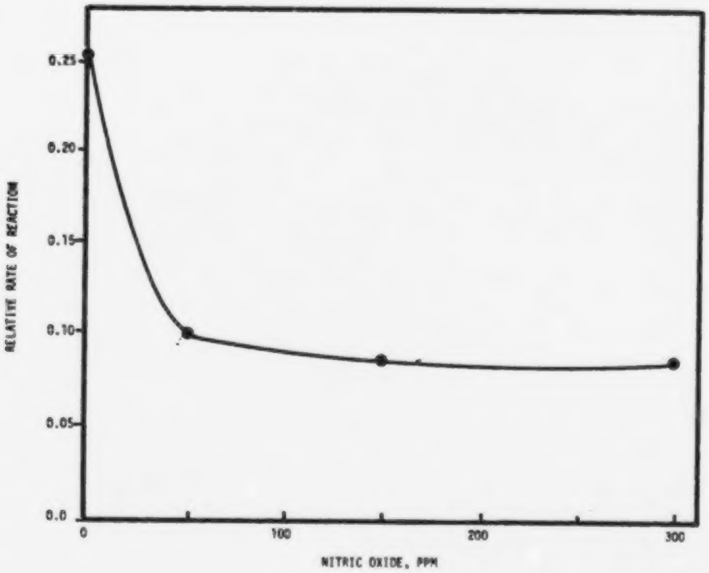


FIGURE 8. Effect of nitric oxide on SO_2 sorption at 200°F.



relating all of the variables affecting SO_2 sorption as given by Equation (1):

$$\left(\begin{matrix}\text{Rate of Acid}\\ \text{Formation}\end{matrix}\right) r_v = 1.59(10^{-4})\, e^{\frac{5520}{T}} \, (SO_2)^{0.4} \, (O_2)^{0.63} (H_2O)^{0.73} \left(1 - \frac{H_2SO_4}{0.38}\right) \qquad (1)$$

This expression can be used in reactor design[2] by integration of the general design expression as given by Equation (2);

$$\text{Space Velocity} = \int_{y_i}^{y_o} \frac{dy}{-r} \qquad (2)$$

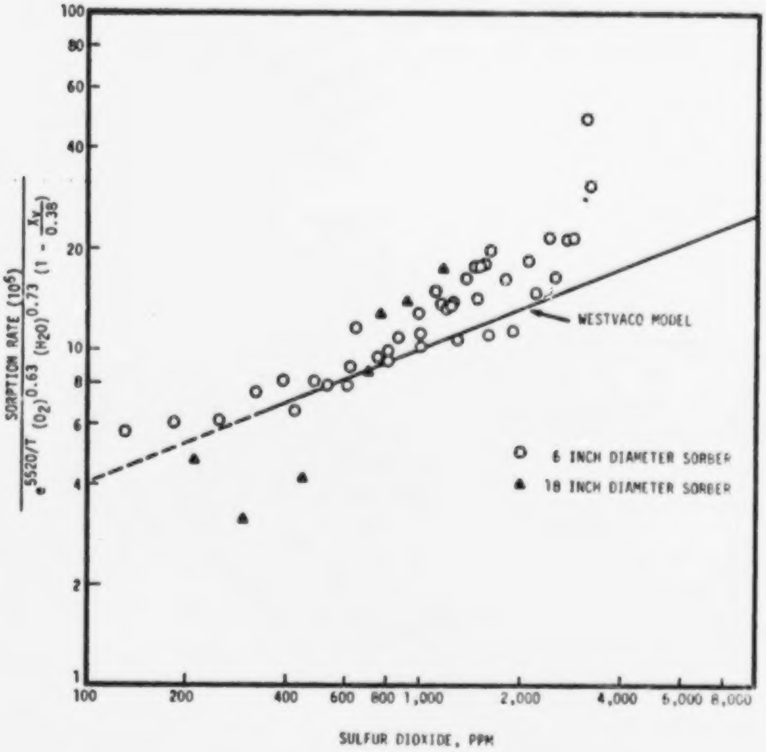
where r is the rate expression (1). For a stagewise fluidized bed with the assumption of complete solids backmixing on each stage and plug flow of the gas, the design relationship reduces to Equation (3):

$$S = 2.65(10^{-4})\, e^{\frac{5520}{T}} \, (O_2)^{0.63} \, (H_2O)^{0.73} \left(1 - \frac{H_2SO_4}{0.38}\right) \left[(y_2)^{0.6} - (y_1)^{0.6}\right] \qquad (3)$$

where y_1 and y_2 are the SO_2 concentrations entering and leaving any particular stage and S is the space velocity for that stage.

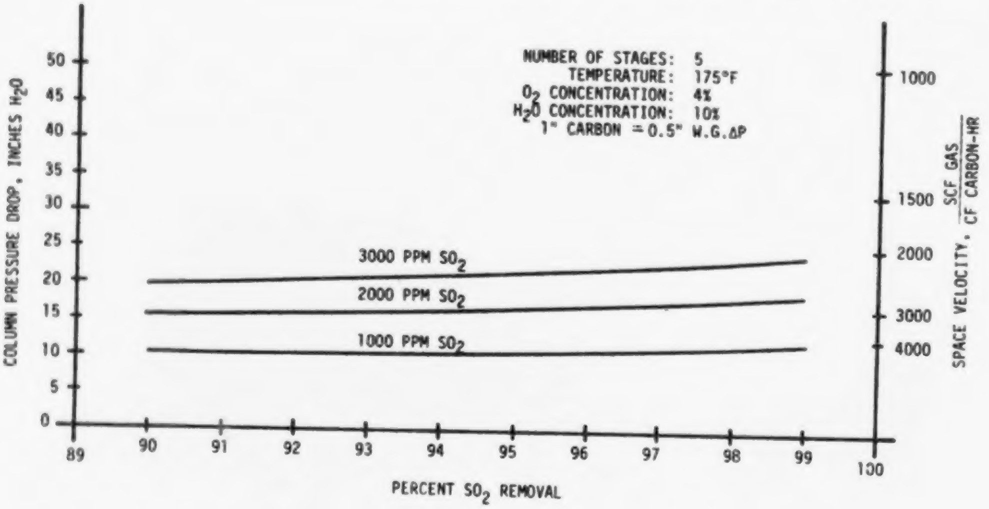
The expression derived from bench scale results were compared with pilot tests in the fluid bed SO_2 sorber operating on actual flue gas and gave good agreement as shown in Figure 9.

FIGURE 9. Comparison of rate model to pilot data.



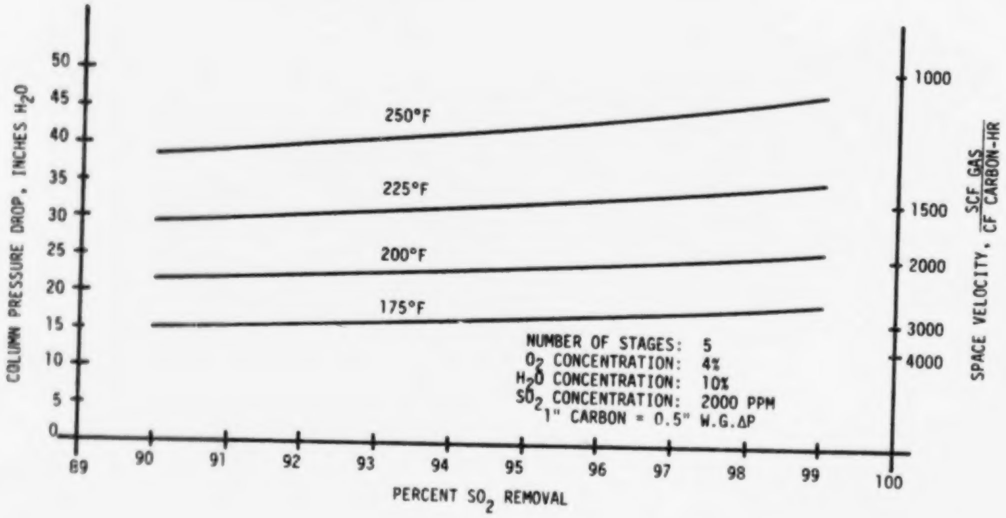
These data can be used to estimate the reactor requirements for a variety of flue gas conditions. Changes in flue gas basically affect the reactor space velocity which is directly related to the pressure drop through the carbon bed depth. Figures 10 to 12 illustrate the

FIGURE 10. Effect of sulfur dioxide concentration in flue gas on pressure drop and space velocity for various levels of SO2 removal.



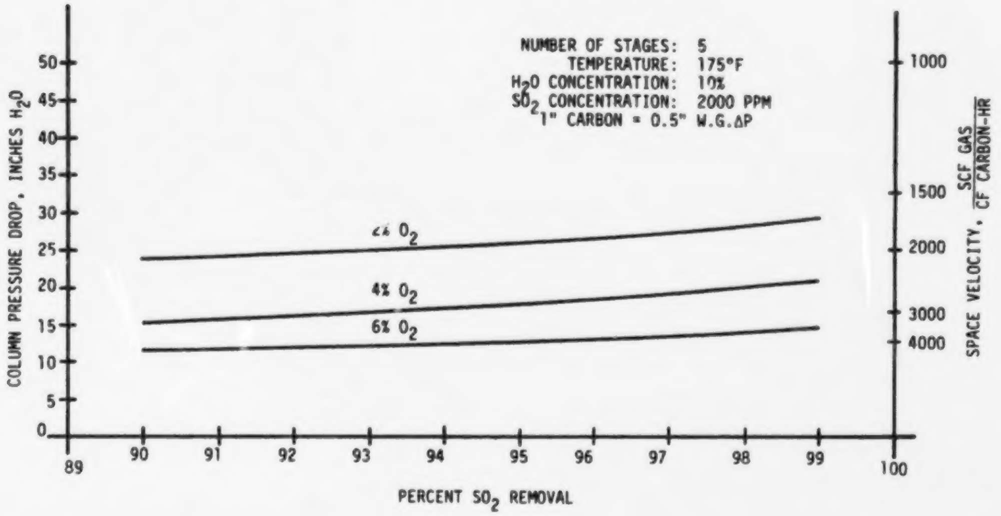
effect on the sorber space velocity and pressure drop for the range of conditions normally encountered in flue gas.

FIGURE 11. Effect of temperature on pressure drop and space velocity for various levels of SO2 removal.



An important characteristic of the system, as demonstrated by the curves, is the little penalty required in terms of pressure drop in order to increase SO_2 removal from 90 - 99%. More details of the rate data and rate model for SO_2 sorption are included in previous publications[3,4].

FIGURE 12. Effect of oxygen concentration in flue gas on pressure drop and space velocity for various levels of SO_2 removal.



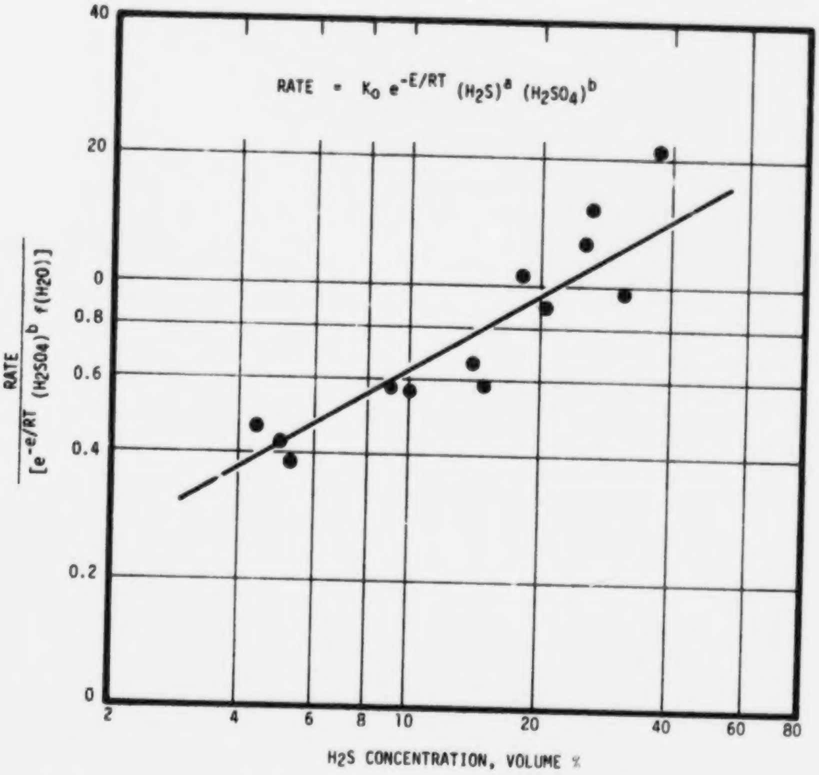
Acid Conversion

The activated carbon from the SO_2 sorber contains sulfuric acid sorbed in the pores of carbon and the acid is converted to elemental sulfur with hydrogen sulfide in the acid converter. Bench scale rate measurements, made over a wide range of conditions, led to a rate model. Equation (4):

$$\text{Rate of Sulfur Formation} = 3.8\, e^{-2644/T} (X_v)^{0.67} (y_{H_2S})^{0.58} \qquad (4)$$

that represented the rate data shown in Figure 13. Using the same assumptions made for the SO_2 sorber as a multistage fluid bed, Equation (4)

FIGURE 13. Comparison of the sulfur generation rate model to the experimental data for 250 to 325°F.



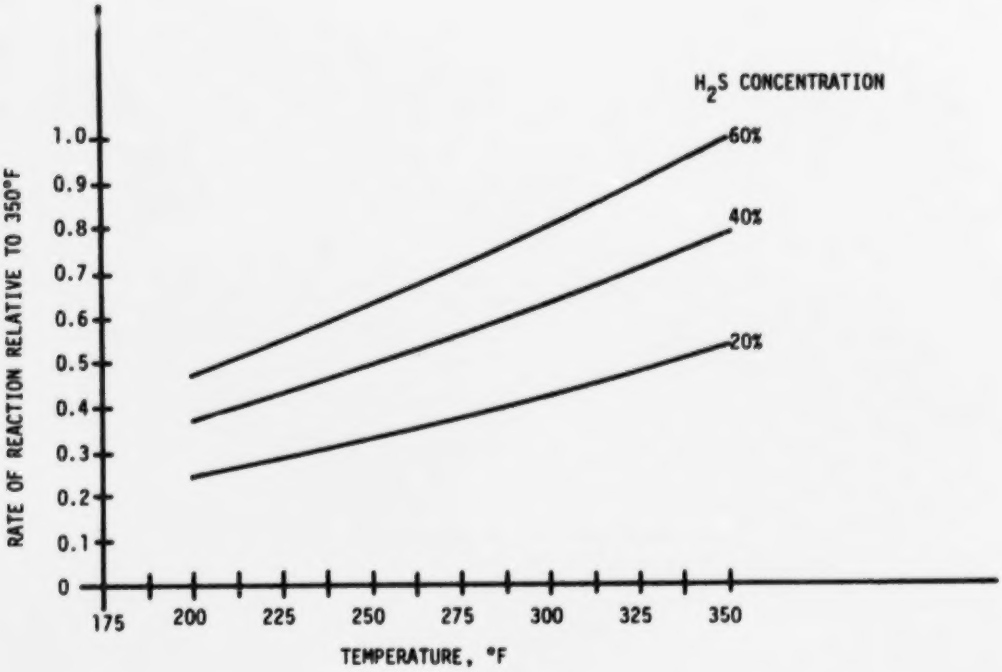
was used to develop the design relationship, Equation (5):

$$\text{Space Velocity} = 9.05\, e^{-2644/T}\, X_v^{0.67} \left[y_2^{0.42} - y_1^{0.42} \right] \qquad (5)$$

where X_v is the acid loading on a stage and y_1 and y_2 are the H_2S concentrations entering and leaving the stage. The design relationship was compared to actual pilot fluid bed operation and predicted results within about 25%.

The relative effects of hydrogen sulfide concentration and temperature on the rate of reaction below 350°F and 60% H_2S are shown in Figure 14. As can be seen, as the temperature or H_2S concentration decreases, the relative rate of reaction also decreases. Although the reaction is not as temperature sensitive as the SO_2 removal, an operating temperature as high as possible is desirable to maximize the space velocity. The upper limit to temperature is about 350°F because acid conversion begins at this temperature; and, for this reason, an operating temperature of about 300°F is normally used. The H_2S concentration on

FIGURE 14. Effect of temperature and H_2S concentration on the relative rate of sulfuric acid conversion to elemental sulfur.



the other hand is a function of the hydrogen concentration to the sulfur stripper/H_2S generator. Typical concentrations from a reformer after being shifted are about 60% and from a gasifier after being shifted about 20%. More information on development of Equation (5) is given in a previous publication[5].

Sulfur Stripping/H2S Generation

During sulfur stripping and H_2S production the sulfur product is vaporized from the carbon and the remainder is reacted with hydrogen to produce the H_2S required for acid conversion. Bench scale testing with sulfur loaded carbon showed that about 7% of the sulfur was chemisorbed and could be removed by reaction with hydrogen. The remainder of the sulfur could be vaporized and recovered as elemental sulfur. Equilibrium experiments showed that the physically adsorbed sulfur isotherm followed the familiar Polanyi-Dubinin relationship as shown below:

$$\ln(L - 7.3) = 4.1 - 0.179(T \log \frac{P_s}{P})^2 \times 10^6$$

where L = lb. S/100 lbs. C

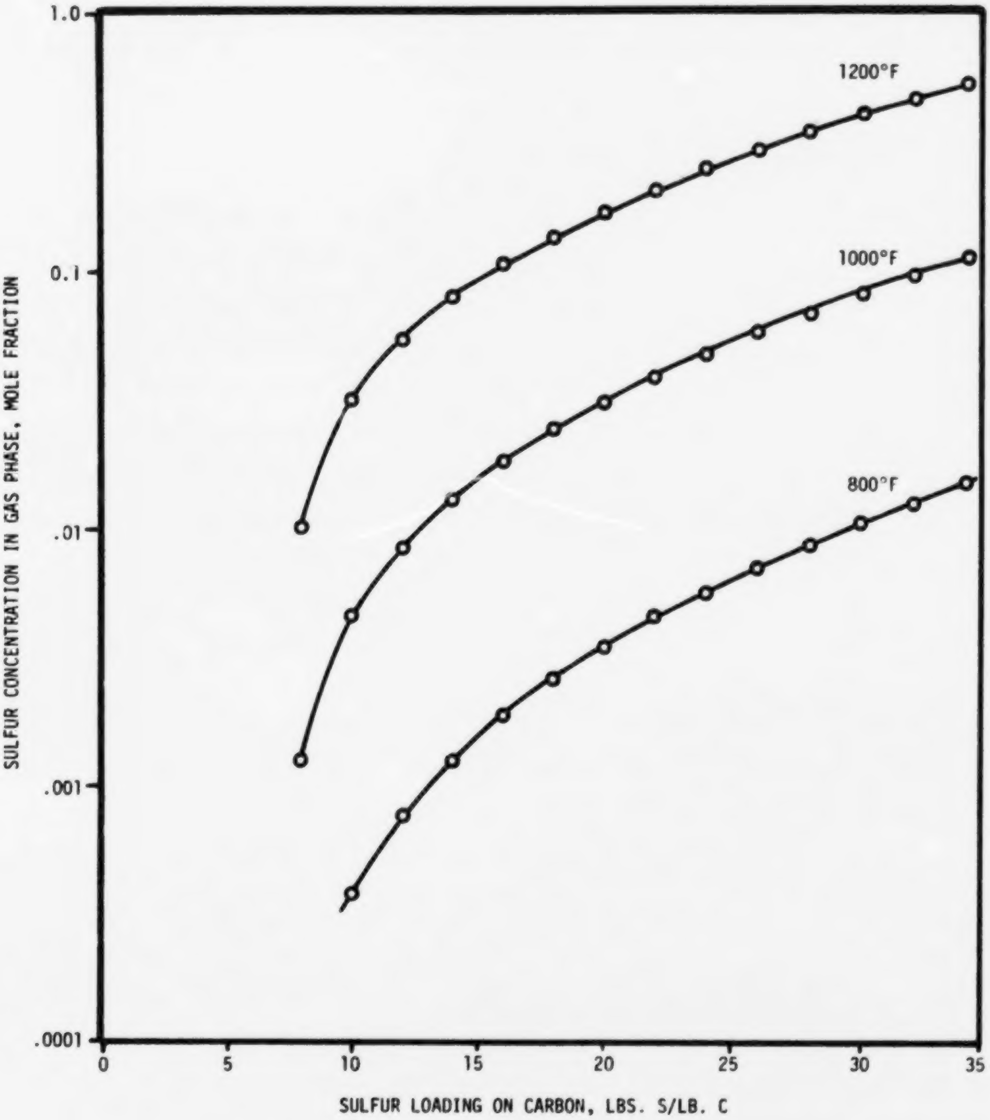
T = °R

P_s = vapor pressure of sulfur, torr

P = vapor pressure of sulfur over carbon, torr.

The effect of loading and temperature upon the concentration of sulfur in the vapor phase over carbon is shown in Figure 15.

Figure 15. Effect of temperature on the equilibrium data of sulfur vapor over activated carbon.



In a continuous system the removal of physically adsorbed sulfur is a function of temperature and residence time and the removal of the chemisorbed sulfur is a function of temperature, hydrogen concentration and contact time.

The results of fluid bed tests summarized in Figures 16 and 17 showed that temperatures of 1000-1200°F were desirable to reduce the residual sulfur loading to acceptable values. Removal of the sulfur is not a strong function of hydrogen concentration as long as sufficient hydrogen is available for reaction with the chemisorbed sulfur.

FIGURE 16. Effect of temperature on sulfur removal in a continuous fluid bed reactor.

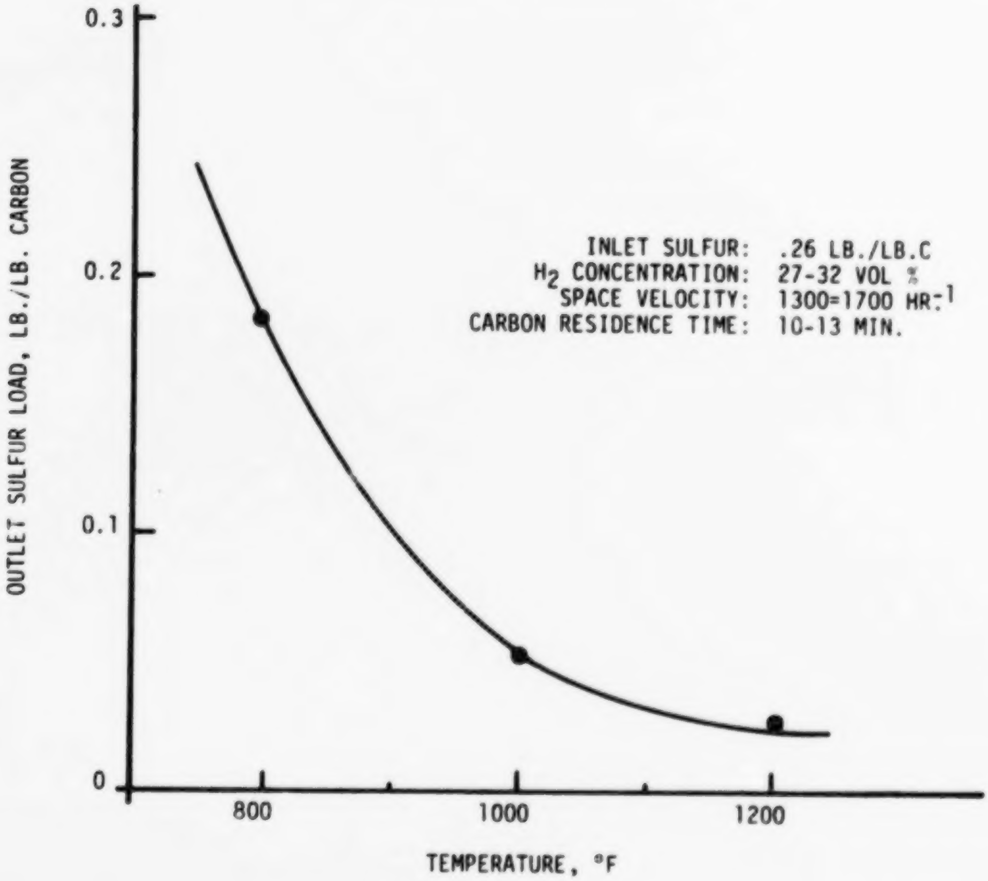
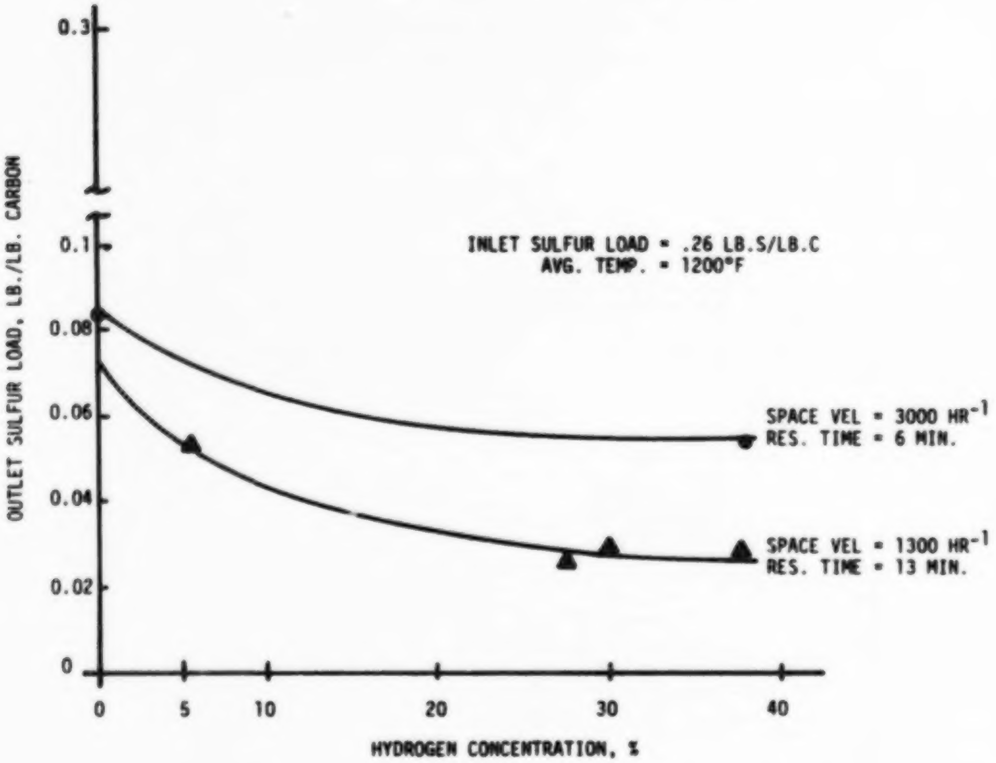


FIGURE 17. Effect of hydrogen concentration on sulfur removal from active carbon in a continuous fluid bed reactor.



Once the sulfur is in the gas phase with hydrogen, reaction occurs to form H_2S required in the acid converter. Studies showed that the conversion rate is expressed by Equation (6):

$$\text{Rate of } H_2S \text{ Formation} = \left[\frac{208(10^7)(v)^{0.5}}{299\ T\ e^{-30645/T} + (v)^{0.5}}\right] e^{-30645/T}\ (S)^{1/2}\ (H_2) \qquad (6)$$

where v = linear gas velocity, ft./sec.

T = temperature, °R

S = sulfur concentration as S_1, volume fraction

H_2 = hydrogen concentration, volume fraction.

The interrelationships of stripping equilibrium and rate and H_2S formation rate are now being combined to develop a method for design of this reactor. The space velocities/conversion relationship measured during separate unit and integral tests, however, provide sufficient information for scale-up under expected conditions which can be refined as modeling techniques improve.

CONTINUED PROCESS DEVELOPMENT - PROTOTYPE

Sufficient information has been developed with the initial integral pilot operation to consider scale-up to a larger unit. The mechanical, adsorptive and catalytic character of the granular activated carbon has been maintained during steady state recycle conditions over an extended period without any significant departure from the initial process concept. Fluidized beds, as used in the integral and pre-integral pilot operation, provide an effective means for gas-solid contacting, even through some solids flow problems were experienced, not unexpected for this size equipment. Undesired side reactions or buildup of trace contaminants were not evident over the 300 hour carbon recycle test period. Although not discussed, the demands on the materials of construction are within those normally encountered in the petroleum industry. Information on basic reaction rates and heats of reaction is available for scale-up which essentially involves expansion of the cross-sectional area of the fluidized reactors since the carbon bed depth should remain essentially the same as in the pilot plant.

In selecting the next size for scale-up, consideration must be given to the type of information required and minimizing risks without committing excessive money. The size of the intermediate unit should permit getting the technical and economic information needed for decisions to proceed to a full plant scale. The prototype should provide specific data on validity of scale-up, performance of materials of construction, process dependability and controllability and performance of off-the-shelf process equipment.

With these factors in mind, a scale-up of about 100 from the present pilot size or a 15 MW equivalent prototype installation is proposed. The flue gas volume rate for the prototype would be 1.2 million scfh compared to the 15,000 scfh of the pilot plant or a 16.3 ft. diameter SO_2 sorber compared to the pilot plant 1.5 ft. diameter sorber.

A parallel continuing process development program while the prototype unit is being constructed and installed would serve a useful purpose. Although major design features of the reactors can be scaled up with some confidence, the effect of internals on the fluidizing mechanics should be prudently determined in mock-up or shop tests. Since there is limited experience in operation of the integral pilot plant, additional performance testing under a variety of conditions would be of value in design and operation of the prototype.

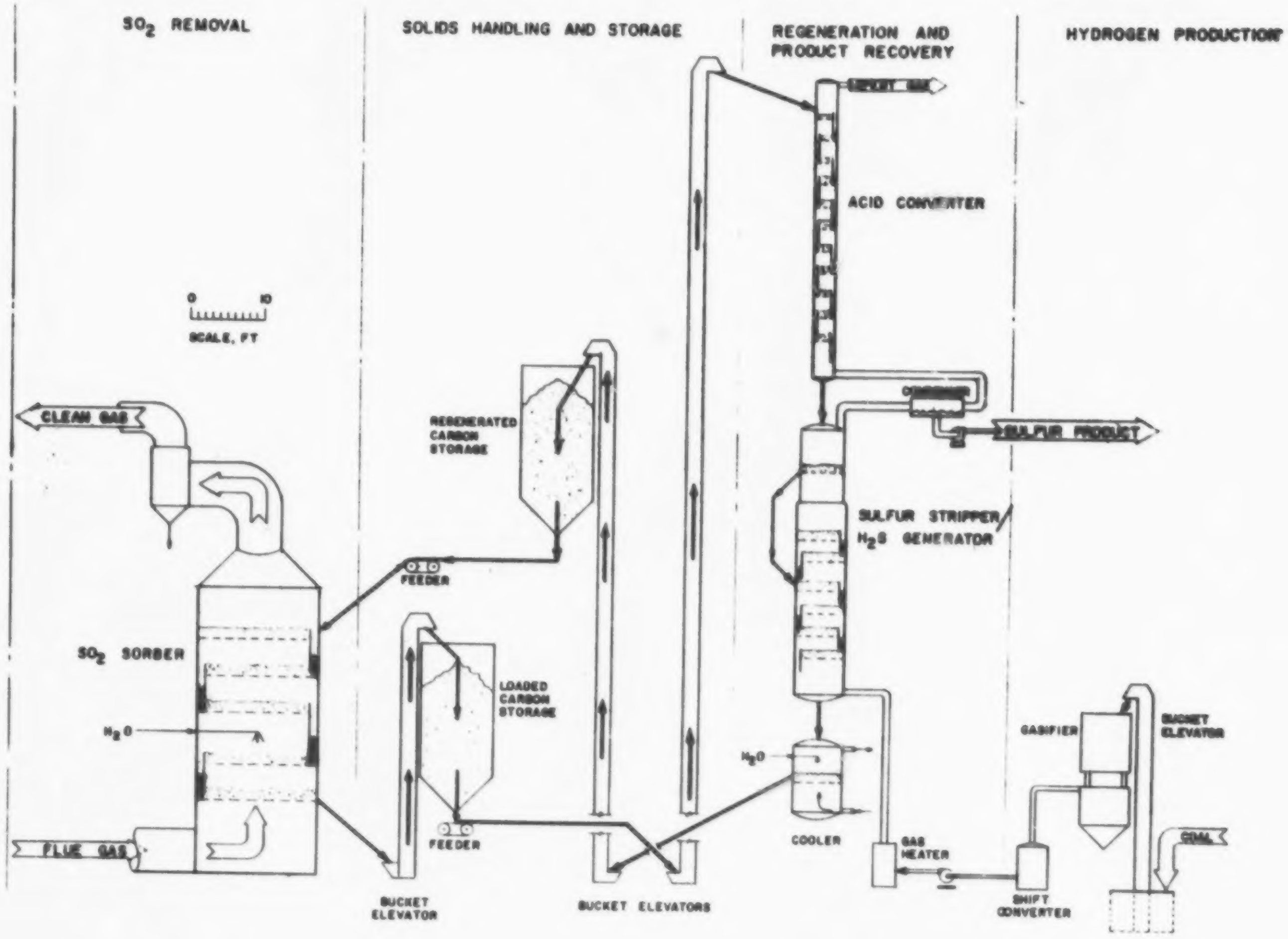
A preliminary prototype design has been prepared based on calculations and the information available from the pilot plant operation. The prototype plant consists of four major components or areas as with the pilot plant:

1. Flue gas scrubbing (dry SO_2 removal)
2. Carbon regeneration and sulfur by-product recovery
3. Reducing gas (hydrogen) production
4. Materials handling and storage.

The basis for the nominal design is 90% removal of SO_2 from a coal fired boiler using 3.5% sulfur coal. The sizes for the major pieces of equipment for the 15 MW prototype have been determined and are presented in Figure 18 in elevation form.

Carbon is transferred at a rate of 3.3 tons/hour between the SO_2 sorber for treatment of 30,000 scfm flue gas and the regeneration reactors for removal and recovery of the elemental sulfur produced at a rate of 1,328 lbs./hr. The transfer system consists of 3 bucket elevators and 2 hoppers for 10 hours of storage for regenerated and acid loaded carbon. The reducing gas is produced in a gas producer with a coal usage of 716 lbs./hr. The equipment and information are shown on the following pages.

FIGURE 18. WESTVACO PROCESS 15 MW PROTOTYPE UNIT


SO_2 REMOVAL
SOLIDS HANDLING AND STORAGE
REGENERATION AND PRODUCT RECOVERY
HYDROGEN PRODUCTION
0
10
SCALE, FT
CLEAN GAS
SO_2 SORBER
H_2O
FLUE GAS
FEEDER
REGENERATED CARBON STORAGE
LOADED CARBON STORAGE
FEEDER
BUCKET ELEVATOR
BUCKET ELEVATORS
SPENT GAS
ACID CONVERTER
CONDENSER
SULFUR PRODUCT
SULFUR STRIPPER/ H_2S GENERATOR
H_2O
COOLER
GAS HEATER
SHIFT CONVERTER
GASIFIER
BUCKET ELEVATOR
COAL

FLUE GAS SO_2 SORBER

GAS RATE:	30,000 SCFM
GAS COMPOSITION:	2,610 PPM SO_2 40 PPM SO_3 4% O_2 10% H_2O
REACTION:	$SO_2 + 1/2\ O_2 \longrightarrow SO_3$ $SO_3 + H_2O \longrightarrow H_2SO_4$ (Sorbed)
DESIGN SO_2 REMOVAL:	90 %
OUTLET CARBON LOADING:	0.22 LB. ACID/LB. C
HEAT RELEASE:	-117,000 BTU/MOL SO_2
OPERATING TEMPERATURE:	150-200°F (SO_2 REMOVAL) 300-350°F (SO_3 REMOVAL)
GAS/SOLID CONTACT:	GAS/SOLID FLUID BED COUNTERCURRENT, 5 STAGES
FLUIDIZING GAS VELOC.:	3 FT./Sec.
SPACE VELOCITY:	2,350 VOL. GAS/VOL. C-HR.
PRESSURE DROP:	31 INCHES W.G.
VESSEL DIAMETER:	18.3 FT.
VESSEL HEIGHT:	50 FT.
MATERIALS OF CONSTRUC.:	MILD STEEL SHELL, ALONIZED STEEL TRAYS

MATERIALS HANDLING AND STORAGE

CARBON RECIRCULATION RATE:	3.3 TONS/HOUR
ACID LADEN CARBON STORAGE:	30 TONS, 10' DIA. x 18.2 FT. CONE BOTTOM TANK, MILD STEEL
REGENERATED CARBON STORAGE:	30 TONS, 10' DIA. x 18.2 FT. CONE BOTTOM TANK, MILD STEEL
VERTICAL ELEVATING:	CONTINUOUS TYPE BUCKET ELEVATORS, MILD STEEL
HORIZONTAL CONVEYING:	BELT OF VIBRATING CONVEYORS, MILD STEEL
FEED RATE CONTROL:	GRAVIMETRIC FEEDERS

REGENERATION

ACID CONVERSION	
INLET GAS RATE:	850 SCFM
H_2S CONCENTRATION:	22%
REACTION:	$H_2SO_4 + 3\ H_2S \longrightarrow 4\ S + 4\ H_2O$
DESIGN ACID CONVERSION:	85%
HEAT RELEASE:	-41,107 BTU/mol acid
OPERATING TEMP.:	300°F
GAS/SOLID CONTACT:	GAS/SOLID FLUID BED, COUNTERCURRENT, 11 STAGES
FLUIDIZING GAS VELOC.:	3 FT./SEC.
SPACE VELOCITY:	460 VOL. GAS/VOL. C-Hr.
PRESSURE DROP:	55 INCHES W.G.
VESSEL DIAMETER:	3 FT.
VESSEL HEIGHT:	30 FT.
MATERIAL OF CONSTRUC.:	ALONIZED MILD STEEL
SULFUR STRIPPING/H_2S PRODUCTION	
GAS RATE:	1,543 SCFM
H_2 CONCENTRATION:	19.4%
REACTIONS:	$H_2SO_4 + 3\ H_2S \longrightarrow 4\ S + 4\ H_2O$ $H_2 + S \longrightarrow H_2S$ $S\downarrow \xrightarrow{\text{Heat}} S\uparrow$
HEAT RELEASE:	-8,667 BTU/mol S ($S \longrightarrow H_2S$)
OPERATING TEMPERATURE:	300-1200°F
GAS/SOLID CONTACT:	GAS/SOLID FLUID BED, COUNTERCURRENT, 7 STAGES
FLUIDIZING GAS VELOC.:	1600 VOL. GAS/VOL. C-Hr.
PRESSURE DROP:	28 INCHES W.G.
VESSEL DIAMETER:	5.8 FT.
VESSEL HEIGHT:	35 FT.
MATERIAL OF CONSTRUC.:	ALONIZED 304 SS
HEAT INPUT:	BY FLUIDIZING GASES, 2 MM BTU/Hr.
CARBON COOLING	
GAS/SOLID CONTACT:	GAS/SOLID FLUID BED, 1 STAGE
HEAT REMOVAL:	1.5 MM BTU/HR. DIRECT H_2O EVAPORATION
CARBON RESIDENCE TIME:	5 MINUTES
VESSEL DIAMETER:	5.8 FT.
VESSEL HEIGHT:	9 FT.
MATERIAL OF CONSTRUC.:	ALONIZED SS

HYDROGEN PRODUCTION

FEED MATERIAL:	BITUMINOUS COAL
FEED RATE:	716 LBS./HR.
GASIFIER	
TYPE:	MOVING BED WITH AGITATOR, STEAM/AIR BLAST
PRODUCTION RATE:	28 CF (H_2 + CO/LB. COAL)
SHIFT CONVERTER	
TYPE:	FIXED BED, 2 STAGES
REACTION:	$H_2O + CO \longrightarrow CO_2 + H_2$
CATALYST VOLUME:	180 FT.^{3}
MATERIAL OF CONSTRUC.:	MILD STEEL

Preliminary process flowsheets and heat and material balances have also been developed for the prototype to permit a detailed design and cost estimate to be prepared.

PROCESS ECONOMICS

The projection of full scale flue gas desulfurization system costs from pilot data is risky at best due to the many uncertainities associated with full scale commercial units. Such an evaluation may, however, provide an indication of the process standing relative to others under development and can help identify critical areas for future development.

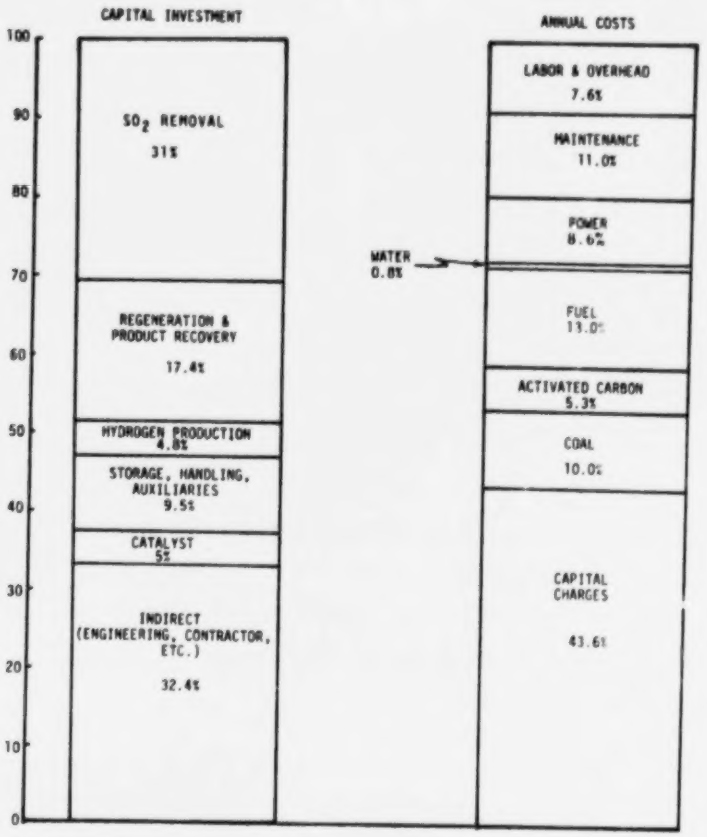
An economic evaluation was prepared for the Westvaco Process by scaling up the 15 MW flowsheet presented earlier to a 250 MW module. A 250 MW module was chosen because this given fluid bed SO_2 sorber sizes comparable to those that have been constructed and operated commercially in solvent vapor recovery. The costs derived from this conceptual design for a 1,000 MW installation comprised of four 250 MW modules is summarized in Table 3.

TABLE 3. Estimated capital and operating costs for 1,000 MW utility boiler.

Investment	Annual Costs
$35/KW	2 Mil/KWH

It is recognized that there are many factors which will undoubtedly affect costs as the process is scaled up. This estimate would seem, however, to indicate that the Westvaco system is competitive with others under development. The cost distribution shown in Figure 19 provides a basis for defining the areas of emphasis in future development.

FIGURE 19. Westvaco process cost distribution.



The largest direct cost items in the investment are the SO_2 removal and carbon regeneration with 31% and 17.4% of the total cost, respectively. These are also the system components for which there is the least full scale knowledge. This suggests that significant attention to the details in this equipment may result in cost reductions.

As might be expected, the charges for the original plant investment are by far the largest annual cost, reaching nearly half of the total. Any possible reduction in the sorber and regenerator costs in particular would have a significant effect on this. Activated carbon make-up charges account for 5.3% of the annual cost under the assumed losses.

Power and fuel costs in the current design comprise nearly 25% of the annual costs. The power costs are, of course, primarily a result of the pressure drop in the SO_2 sorber. A reduction in the power consumption would be most affected by further improvements in the efficiency of the activated carbon, since the carbon inventory and consequently the pressure drop of the SO_2 sorber are directly related to carbon efficiency.

The fuel costs result primarily from the need to heat the activated carbon and sulfur to the stripping temperature. No credit was taken in this evaluation for steam produced during sulfur product condensation which will partially offset fuel costs. There is also the potential for heat recovery from the activated carbon but this must be investigated for the trade-off between the additional equipment costs and the fuel savings. No credit for sulfur recovery was assumed.

Consideration of these cost factors should be included in the design and operating test objectives of the prototype program.

CONCLUSIONS

The general objectives of the program were to develop further information on each process step, to demonstrate the technical feasibility of the entire process and to evaluate the performance of the carbon under extended recycling conditions in an integrated pilot plant using flue gas from an oil fired boiler.

The basic conclusions reached on the results and information to date are:

1. Granular activated carbon of the type used can effectively remove SO_2 from flue gas and can be regenerated satisfactorily over a repeated number of

cycles without reduction in activity or an unacceptable physical loss through chemical reaction or mechanical attrition.

2. Information has been developed on each of the three unit process steps, SO_2 sorption, acid conversion and S stripping/H_2S generation, to define the principal variables affecting the process chemistry and their correlations in regard to rate of reaction.
3. An acceptable sulfur product can be produced by the process with H_2S as an internally generated intermediate reductant.
4. Use of fluidized beds present a viable and attractive method of gas-solids contacting although other contacting means are also applicable.
5. Operation of the integral pilot plant over the limited time did not appear to present any problems in regard to control of the process.
6. Sufficient information has been generated on the performance of the activated carbon, process chemistry and pilot operation to proceed to the next stage of development.

RECOMMENDATIONS

Based on the above conclusions it is proposed that scale-up to a larger prototype plant be considered as the next step toward a commercial plant.

ACKNOWLEDGEMENTS

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